

Supporting Information

Capture CO₂ in Air to 4,5-Disubstituted Furan-2(5*H*)-ones

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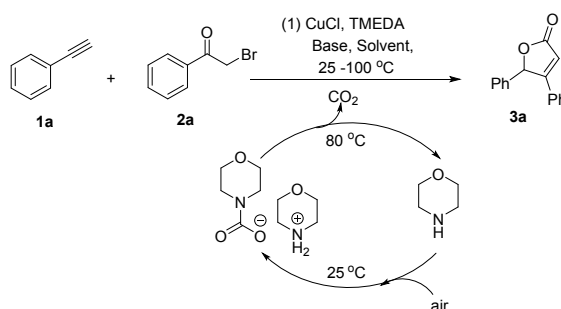
I. General Information

The starting materials were commercially available and all the reactions were carried out in dried glasswares with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ at 400 MHz or 500 MHz NMR spectrometer. The chemical shifts (δ) were referenced to TMS. Melting points were measured with a micro melting point apparatus. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer equipped with EI or ESI ionization source. Agilent 1100 high performance liquid chromatography (HPLC) equipped with an analytical RP-18 column

II. General Experimental Procedure.

(1) Screening the Optimal Conditions

Table S1 Screening the Optimal Conditions ^[a]



Entry	Base	Solvent	Yield ^[b]
1	K_3PO_4	DMF	N.R.
2	K_3PO_4	DMSO	N.R.
3	K_3PO_4	DMAc	N.R.
4	K_3PO_4	Toluene	N.R.
5	K_3PO_4	THF	16%
6	K_3PO_4	MeCN	25%
7	K_2CO_3	MeCN	13%
8	Cs_2CO_3	MeCN	12%
9	KOAc	MeCN	38%
10	Et_3N	MeCN	26%
11	DBU	MeCN	20%
12 ^[c]	KOAc	MeCN	69%
13 ^{[c][d]}	KOAc	MeCN	40%

^[a] One-pot one-step reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), CuCl (2.0 mol%), TMEDA (*N, N, N', N'*-tetramethylethylenediamine) (1.5 mol%), Base (5 mmol), CO_2 (ambient pressure) from an aqueous capturing, solvent (5 mL) at 25 °C for 16 h and then stirring continued at 100 °C for 10 h. ^[b] Isolated yield (based on **1a**). ^[c] One-pot two-step reaction conditions: K_3PO_4 (1.2 mmol), CO_2 (ambient pressure) from an aqueous capturing solution, DMF (5 mL), room temperature (about 25 °C), schlenk tube 16 h. After extracting offered the crude product. Then KOAc (4 mmol) and the crude product were dissolved in anhydrous MeCN (5 mL) and stirred at 100 °C schlenk tube for 10 h under nitrogen atmosphere in the second step. ^[d] CuCl (2.0 mol%) and TMEDA (1.5 mol%) were added in the second step.

(2) Determination of glyoxylic acid (6a) by HPLC

Standard sample (40% in water) was analyzed under the following conditions: delivery system, MeOH (A)–0.1% H₂O (aq) (B), 10% A/B to 45% A/B in 18 min, and 7 min to 95% A/B; amount injected, 1 mg/20 μ L (MeOH) $\times$ 3; flow rate, 0.6 mL/min; monitored at 280 nm.

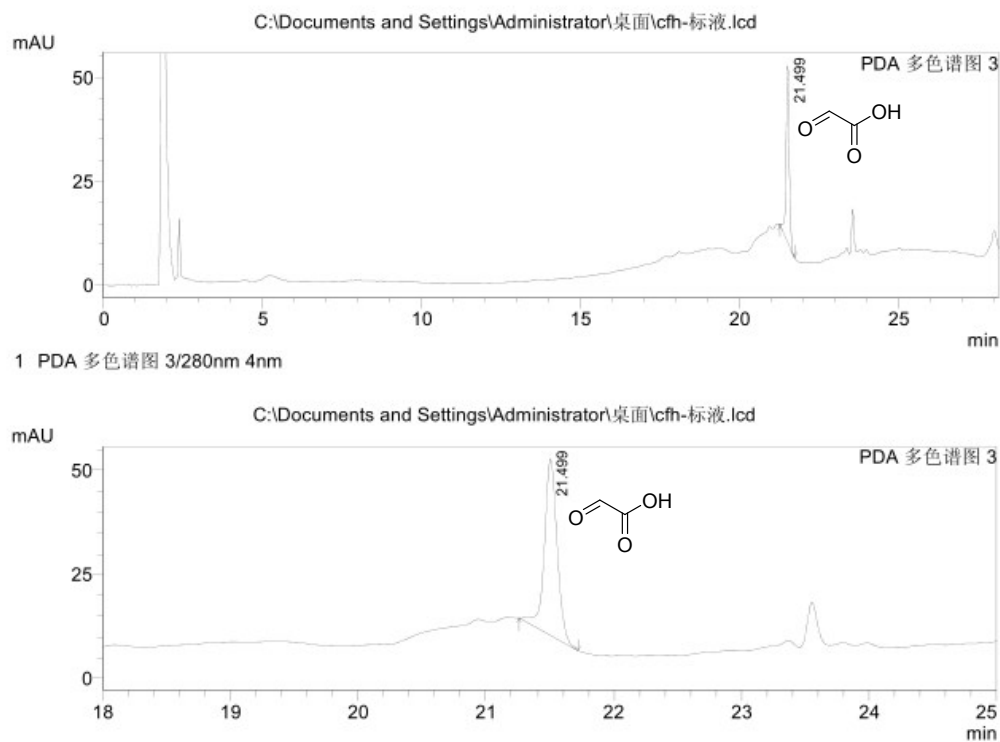


Fig.1 Chromatogram of glyoxylic acid (40% in water) standard sample

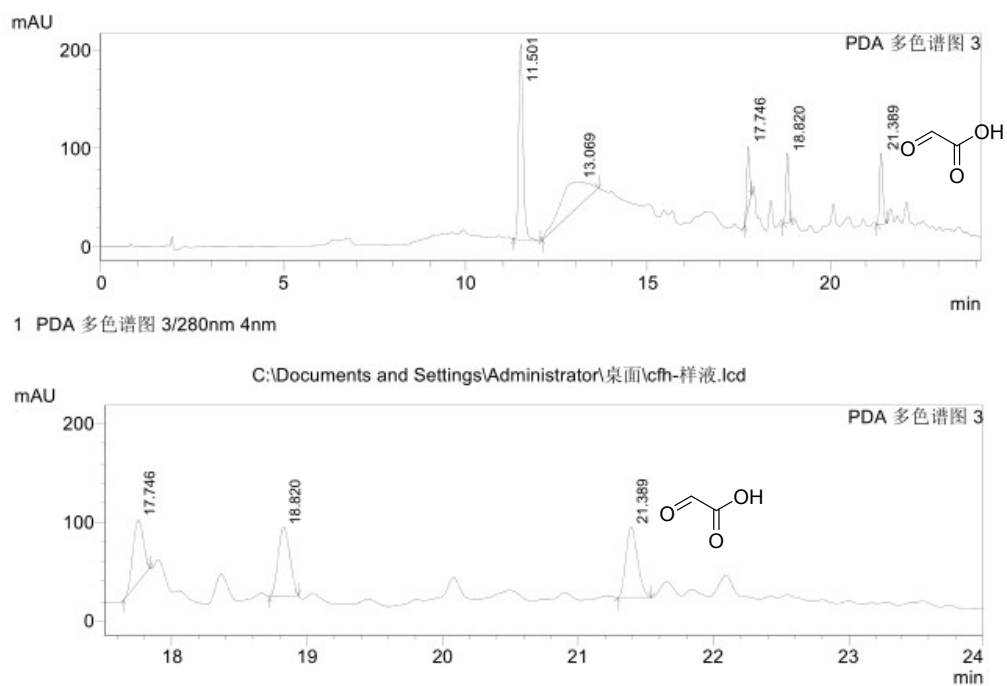


Fig.2 Chromatogram of reaction system

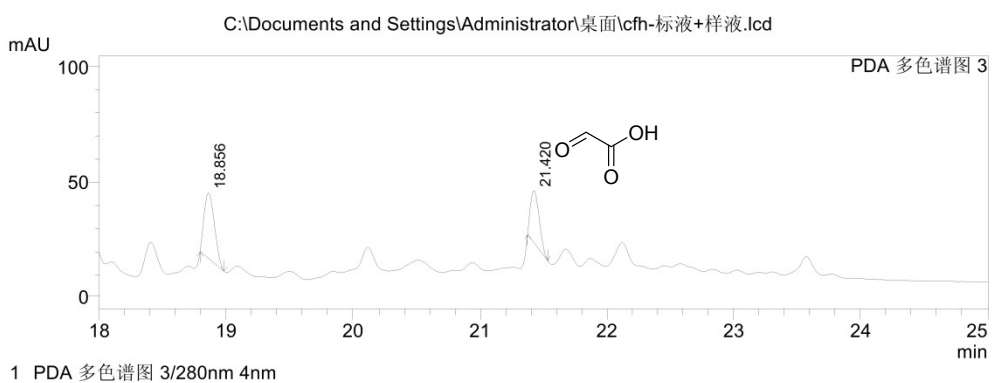
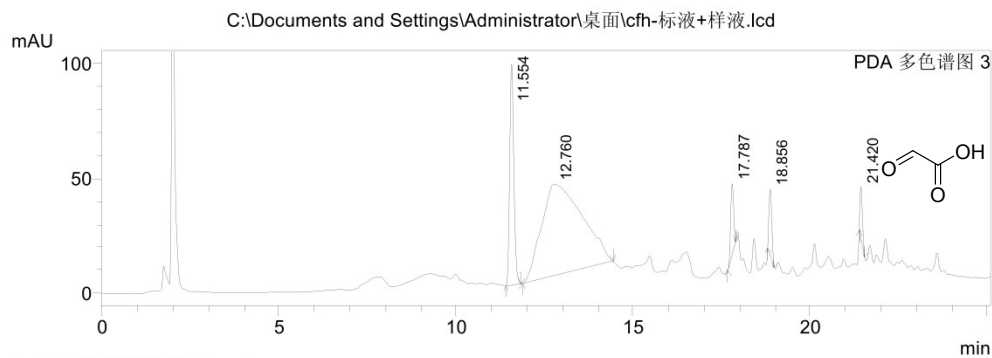
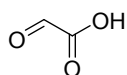


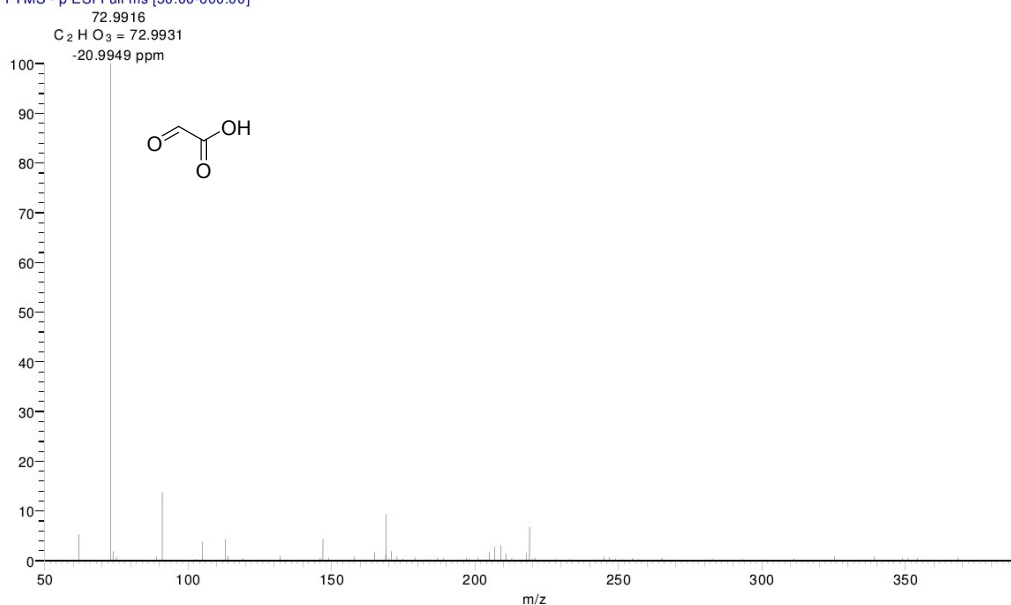
Fig.3 Chromatogram of the mixture of glyoxylic acid standard sample glyoxylic acid (40% in water) and reaction system (1:1)

(2) Determination of glyoxylic acid by HRMS



2-Oxoacetic acid (6a): HRMS (ESI) calcd for $C_2H_2O_3[M-H]^-$ 72.9926, found 72.9931.

cfh-3-48_160801165716 #16 RT: 0.15 AV: 1 NL: 5.86E8
T: FTMS - p ESI Full ms [50.00-600.00]



(3) Capture and release of carbon dioxide in air³

The air was bubbled by pressure pump in 100 mL aqueous morpholine solution (0.4 mol/L) in a Schlenk flask at 25 °C. Stop keeping bubbling until a large number of white solid generated. The CO₂-saturated solution could be stored for more than a week at room temperature and used when needed. The flask with CO₂-saturated solution was linked to a reflux condenser. The top of reflux condenser and the target reaction flask was connected by a gas bottle equipped with concentrated sulfuric acid (98%). The CO₂-saturated solution was heated to 80 °C about 3 min to pushing the air out of the device through the vent line on the target reaction flask. Then the vent line was equipped with a balloon which was purged by pure CO₂. Keeping heating until no more CO₂ introduced from the aqueous morpholine solution (Figures 4 and 5).

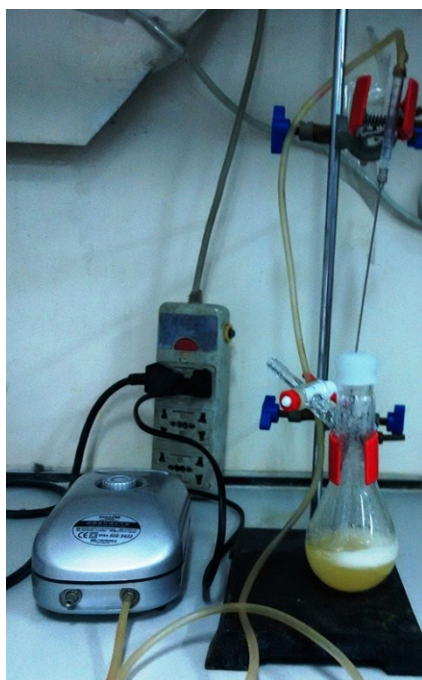
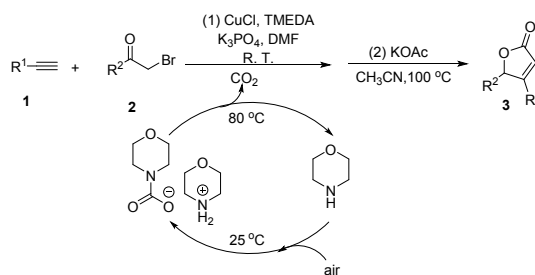


Figure 4. CO₂ capture process

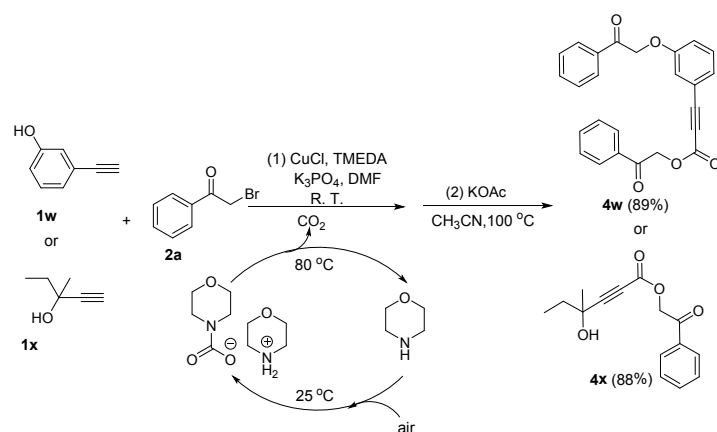


Figure 5. Release process of CO₂

(4) Synthesis of 4,5-disubstituted furan-2(5H)-ones from CO₂.^{3,4}



1 (1.0 mmol), **2** (1.2 mmol), CuCl (2.0 mol%), TMEDA (1.5 mol%), K₃PO₄ (1.2 mmol) were dissolved in DMF (5 mL) and stirred in a Schlenk tube. The CO₂ from the captured solution was introduced to reaction tube for 3 min to pushing the air out of the device through the vent line on schlenk tube. Then the vent line was equipped with a balloon which was purged by pure CO₂. Keep heating until no more CO₂ introduced from the aqueous morpholine solution. The reaction mixture was stirred at room temperature (about 25 °C) for 16 h under an atmosphere of CO₂. After the Schlenk tube was cooled to room temperature, water was added into the mixture, and extracted with ethyl acetate three times. The combined organic layer was dried by anhydrous MgSO₄, and the solvent was removed under vacuum. The crude product was directly applied to second step reaction without further purified. In the second step reaction, the crude product and KOAc (4 mmol) were dissolved in anhydrous MeCN (5 mL) and stirred in a Schlenk tube at 100 °C for 10 h under a nitrogen atmosphere. Upon completion of the reaction as indicated by TLC, the mixture was filtered, washed with diethyl ether, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the pure product. Unfortunately, the alkynes with hydroxyl groups, such as 3-ethynylphenol and 3-methylpent-1-yn-3-ol, failed to afford the desired products but gave product **4w** and **4x** in high yields.



The reaction scheme illustrates the synthesis of furan derivatives **3a** and **3b** from phenylacetylene (**1a**).

1a (Phenylacetylene) is converted to **2a** (2-bromo-1-phenylethan-1-one) and **2v** (2-bromo-1-phenylethan-1-one, isomer) via a reaction with (1) CuCl, TMEDA, K₃PO₄, DMF, R. T., and CO₂ at 80 °C.

2a is cyclized to **3a** (2-phenyl-2,5-dihydrofuran) using (2) KOAc, CH₃CN, 100 °C, 10 h, yielding **3a** (83%).

2v is cyclized to **3b** (2-phenyl-2,5-dihydrofuran) using (2) KOAc, CH₃CN, 100 °C, 6 h, yielding **3b** (41%).

2v is also cyclized to **3c** (2-phenyl-2,5-dihydrofuran) using (2) KOAc, CH₃CN, 100 °C, 10 h, yielding **3c** (48%).

3c is further cyclized to **3d** (2-phenyl-2,5-dihydrofuran) using (2) KOAc, CH₃CN, 100 °C, 10 h, yielding **3d** (81%).

1a (1.0 mmol), **2a** (1.2 mmol), CuCl (2.0 mol%), TMEDA (1.5 mol%), K₃PO₄ (1.2 mmol) were dissolved in DMF (5 mL) and stirred in a Schlenk tube. The CO₂ from the captured solution was introduced to reaction tube for 3 min to pushing the air out of the device through the vent line on schlenk tube. Then the vent line was equipped with a balloon which was purged by pure CO₂. Keep heating until no more CO₂ introduced from the aqueous morpholine solution. The reaction mixture was stirred at room temperature (about 25 °C) for 16 h under an atmosphere of CO₂. After the Schlenk tube was cooled to room temperature, water was added into the mixture, and extracted with ethyl acetate three times. The combined organic layer was dried by anhydrous MgSO₄, and the solvent was removed under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the pure product **4a** (86%).

4a (0.8 mmol) and KOAc (3.2 mmol) were dissolved in anhydrous MeCN (5 mL) and stirred in a Schlenk tube at 100 °C for 10 h under a nitrogen atmosphere. Upon completion of the reaction as indicated by TLC, the mixture was filtered, washed with diethyl ether, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the pure product **3a** (83%).

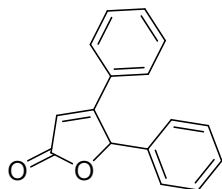
1a (2.0 mmol), **2v** (2.4 mmol), CuCl (2.0 mol%), TMEDA (1.5 mol%), K₃PO₄ (2.4 mmol) were dissolved in DMF (10 mL) and stirred in a Schlenk tube. The CO₂ from the captured solution was

introduced to reaction tube for 3 min to pushing the air out of the device through the vent line on schlenk tube. Then the vent line was equipped with a balloon which was purged by pure CO₂. Keep heating until no more CO₂ introduced from the aqueous morpholine solution. The reaction mixture was stirred at room temperature (about 25 °C) for 16 h under an atmosphere of CO₂. After the Schlenk tube was cooled to room temperature, water was added into the mixture, and extracted with ethyl acetate three times. The combined organic layer was dried by anhydrous MgSO₄, and the solvent was removed under vacuum. The crude product was directly applied to second step reaction without further purified. In the second step reaction, the crude product and KOAc (8 mmol) were dissolved in anhydrous MeCN (10 mL) and stirred in a Schlenk tube at 100 °C for 6 h under a nitrogen atmosphere. Upon completion of the reaction as indicated by TLC, the mixture was filtered, washed with diethyl ether, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the pure products **3a** (41%) and **5v** (48%).

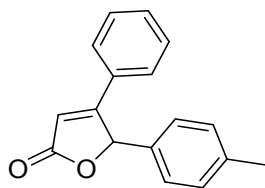
Synthesis of 4,5-Diphenylfuran-2(5H)-one **3a from 5-acetyl-4,5-diphenylfuran-2(5H)-one (**5v**)**

5v (0.8 mmol) and KOAc (3.2 mmol) were dissolved in anhydrous MeCN (5 mL) and stirred in a Schlenk tube at 100 °C for 10 h under a nitrogen atmosphere. Upon completion of the reaction as indicated by TLC, the mixture was filtered, washed with diethyl ether, and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the pure product **3a** (81%).

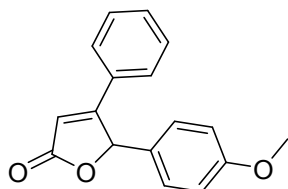
III. Analytical Data for All Compounds



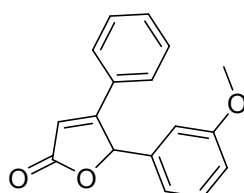
4,5-Diphenylfuran-2(5H)-one (3a**).**¹ Yellow solid, mp 148-150 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.42 (m, 2H), 7.37-7.33 (m, 8H), 6.55 (d, *J* = 1.4 Hz, 1H), 6.33 (d, *J* = 1.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 172.6, 165.8, 134.8, 131.2, 129.5, 129.0, 127.8, 127.5, 114.5, 84.2, 77.3, 76.8; HRMS (EI) for C₁₆H₁₂O₂ (M⁺): calcd. 236.0837, found 236.0838.



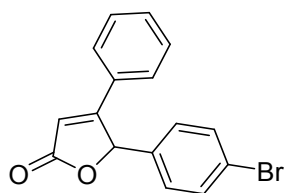
4-Phenyl-5-(p-tolyl)furan-2(5H)-one (3b).¹ Yellow solid, mp 129-130 °C; ¹H NMR(400 MHz, DMSO-*d*₆) δ 7.61 (d, *J* = 5.5 Hz, 2H), 7.40-7.35 (m, 3H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 1.3 Hz, 1H), 6.76 (d, *J* = 1.5 Hz, 1H), 2.24 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 173.0 166.8, 139.0, 133.2, 131.6, 130.0 (2C), 129.3, 128.4, 128.1, 114.7, 83.4, 21.2; HRMS (EI) for C₁₇H₁₄O₂ (M⁺): calcd. 250.0994, found 250.0995.



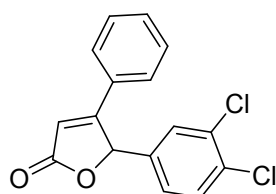
5-(4-Methoxyphenyl)-4-phenylfuran-2(5H)-one (3c). Yellow solid, mp 131-133 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.40 (m, 2H), 7.38-7.31 (m, 3H), 7.21-7.19 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 1.6 Hz, 1H), 6.30 (d, *J* = 1.5 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 165.8, 139.6, 131.9, 131.2, 129.8 (2C), 129.0, 127.8, 127.5, 114.6, 84.3, 21.2; HRMS (EI) for C₁₇H₁₄O₃ (M⁺): calcd. 266.0943, found 266.0945.



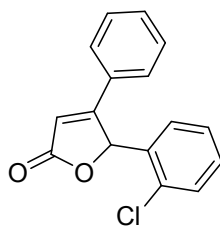
5-(3-Methoxyphenyl)-4-phenylfuran-2(5H)-one (3d). Yellow solid, mp 130-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 5H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.83 (m, 2H), 6.78-6.76 (m, 1H), 6.48 (d, *J* = 1.5 Hz, 1H), 6.23 (d, *J* = 1.3 Hz, 1H), 3.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 165.7, 160.0, 136.3, 131.2, 130.1, 129.6, 129.0, 127.5, 120.2, 114.9, 114.5, 113.4, 84.2, 55.2; HRMS (EI) for C₁₇H₁₄O₃ (M⁺): calcd. 266.0943, found 266.0944.



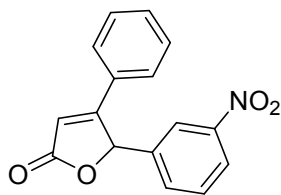
5-(4-Bromophenyl)-4-phenylfuran-2(5H)-one (3e). Yellow solid, mp 131-133 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.64-7.55 (m, 4H), 7.37 (m, 5H), 6.96-6.91 (m, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 172.8, 166.5, 135.6, 132.5, 131.8, 130.4, 129.9, 129.4, 128.4, 123.1, 114.9, 82.6; HRMS (EI) for $\text{C}_{16}\text{H}_{11}\text{BrO}_2$ (M^+): calcd. 313.9942, found 313.9943.



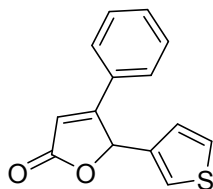
5-(3,4-Dichlorophenyl)-4-phenylfuran-2(5H)-one (3f).¹ Yellow solid, mp 121-123 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.75 (d, $J = 2.1$ Hz, 1H), 7.65-7.61 (m, 3H), 7.43 (m, 3H), 7.36 (m, 1H), 6.96 (d, $J = 1.6$ Hz, 1H), 6.86 (d, $J = 1.6$ Hz, 1H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 172.6, 166.0, 137.2, 132.6, 132.2, 131.9 (2C), 130.4, 129.7, 129.5, 128.3 (2C), 115.2, 81.7; HRMS (EI) for $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{O}_2$ (M^+): calcd. 304.0058, found 304.0057.



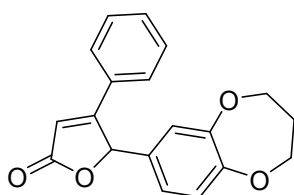
5-(2-Chlorophenyl)-4-phenylfuran-2(5H)-one (3g). Yellow solid, mp 125-127 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.57-7.53 (m, 3H), 7.44-7.38 (m, 4H), 7.31 (m, 1H), 7.21 (d, $J = 7.4$ Hz, 1H), 7.04 (dd, $J = 6.5, 1.7$ Hz, 2H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 172.7, 166.1, 134.1, 133.2, 131.9 (2C), 130.8, 130.0, 129.5, 128.7, 128.1, 115.9, 80.4; HRMS (EI) for $\text{C}_{16}\text{H}_{11}\text{ClO}_2$ (M^+): calcd. 270.0448, found 270.0449.



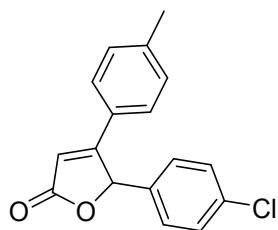
5-(4-Nitrophenyl)-4-phenylfuran-2(5H)-one (3h).¹ Yellow solid, mp 143-144 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.33 (t, *J* = 2.0 Hz, 1H), 8.21 (m, 1H), 7.84-7.80 (m, 1H), 7.70-7.64 (m, 3H), 7.44-7.39 (m, 3H), 7.05 (d, *J* = 1.6 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100MHz, DMSO-*d*₆) δ 172.6, 166.3, 148.6, 138.3, 134.4, 131.9, 131.4, 129.6 (2C), 128.4, 124.9, 123.2, 115.3, 81.9; HRMS (EI) for C₁₆H₁₁NO₄ (M⁺): calcd. 281.0688, found 281.0689.



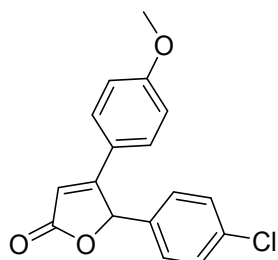
4-Phenyl-5-(thiophen-3-yl)furan-2(5H)-one (3i). Brown solid, mp 140-141 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.39 (m, 2H), 7.38-7.30 (m, 4H), 7.24-7.21 (m, 1H), 6.91 (m, 1H), 6.47 (d, *J* = 1.5 Hz, 1H), 6.43 (d, *J* = 1.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 165.5, 135.7, 131.3, 129.6, 128.9, 127.4, 127.0, 125.9, 125.6, 114.2, 79.1; HRMS (EI) for C₁₄H₁₀O₂S (M⁺): calcd. 242.0402, found 242.0403.



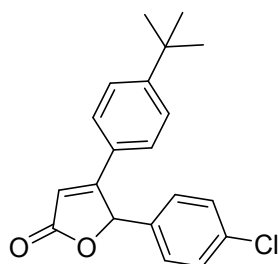
5-(3,4-Dihydro-2H-benzo[b][1,4]dioxepin-7-yl)-4-phenylfuran-2(5H)-one (3j). Yellow solid, mp 147-149 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.32 (m, 5H), 6.94-6.87 (m, 3H), 6.52 (d, *J* = 1.5 Hz, 1H), 6.23 (d, *J* = 1.5 Hz, 1H), 4.19 (m, 4H), 2.19-2.13 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 172.5, 165.5, 152.1, 151.3, 131.2, 129.8, 129.6, 129.0, 127.5, 123.0, 122.2, 121.1, 114.5, 83.6, 70.4 (2C), 31.4; HRMS (EI) for C₁₉H₁₆O₄ (M⁺): calcd. 308.1049, found 308.1050.



5-(4-Chlorophenyl)-4-(p-tolyl)furan-2(5H)-one (3k).¹ Yellow solid, mp 135-137 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 0.8 Hz, 1H), 6.32 (s, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 165.5, 142.1, 135.5, 133.7, 129.8, 129.3 (2C), 127.4, 126.6, 113.6, 83.2, 21.4; HRMS (EI) for C₁₇H₁₃ClO₂ (M⁺): calcd. 284.0604, found 284.0604.

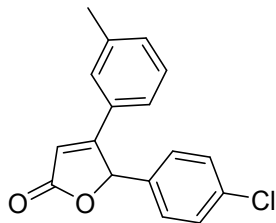


5-(4-Chlorophenyl)-4-(4-methoxyphenyl)furan-2(5H)-one (3l).¹ Yellow solid, mp 138-139 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.28 (m, 4H), 7.24 (m, 2H), 6.84-6.81 (m, 2H), 6.41 (d, *J* = 1.4 Hz, 1H), 6.25 (d, *J* = 1.3 Hz, 1H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.7, 165.0, 162.0, 135.4, 133.8, 129.2 (2C), 121.8, 114.4, 112.1, 83.1, 55.3; HRMS (EI) for C₁₇H₁₃ClO₃ (M⁺): calcd. 300.0553, found 300.0551.

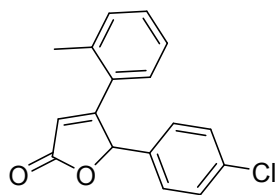


4-(4-(*tert*-Butyl)phenyl)-5-(4-chlorophenyl)furan-2(5H)-one (3m). Yellow solid, mp 141-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (t, *J* = 2.9 Hz, 4H), 7.32-7.27 (m, 4H), 6.52 (d, *J* = 1.5 Hz, 1H), 6.31 (d, *J* = 1.3 Hz, 1H), 1.28 (d, *J* = 1.2 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 165.4, 155.1, 135.4, 133.7, 129.2(2C), 127.3, 126.5, 126.0, 113.7, 83.2, 34.8, 30.8; HRMS (EI) for

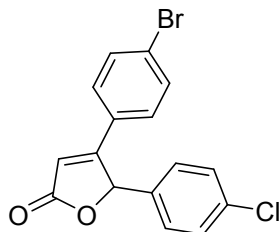
$C_{20}H_{19}ClO_2$ (M^+): calcd. 326.1074, found 326.1073.



5-(4-Chlorophenyl)-4-(m-tolyl)furan-2(5H)-one (3n).¹ Yellow solid, mp 135-137 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.49 (s, 1H), 7.45-7.33 (m, 5H), 7.29-7.22 (m, 2H), 6.88 (d, J = 1.6 Hz, 1H), 6.82 (d, J = 1.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 173.0, 166.9, 138.9, 135.3, 134.5, 132.5, 130.0 (2C), 129.7, 129.4, 128.9, 125.6, 114.7, 82.6, 21.3; HRMS (EI) for $C_{17}H_{13}ClO_2$ (M^+): calcd. 284.0604, found 284.0603.

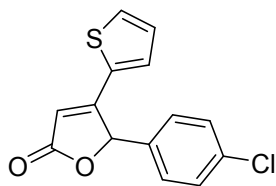


5-(4-Chlorophenyl)-4-(o-tolyl)furan-2(5H)-one (3o). Yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 3H), 7.25-7.18 (m, 2H), 7.16-7.13 (m, 2H), 7.11 (m, 1H), 6.35 (d, J = 1.5 Hz, 1H), 6.31 (d, J = 1.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 167.1, 136.4, 135.1, 132.9, 131.4, 130.1, 129.8, 129.1, 128.2, 127.9, 126.1, 118.0, 84.7, 21.0; HRMS (EI) for $C_{17}H_{13}ClO_2$ (M^+): calcd. 284.0604, found 284.0606.

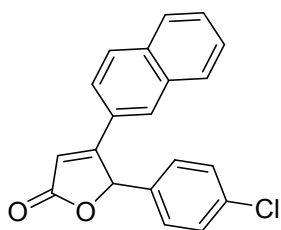


4-(4-Bromophenyl)-5-(4-chlorophenyl)furan-2(5H)-one (3p). Yellow solid, mp 133-135 °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.35 (m, 6H), 7.30-7.27 (m, 2H), 6.59 (d, J = 1.5 Hz, 1H), 6.35 (d, J = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 165.5, 135.6, 133.4, 131.4, 129.4(2C), 129.1(2C), 127.5, 114.7, 83.3; HRMS (EI) for $C_{16}H_{10}BrClO_2$ (M^+): calcd. 347.9553, found

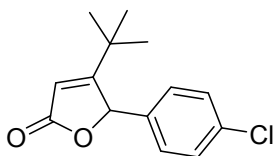
347.9553.



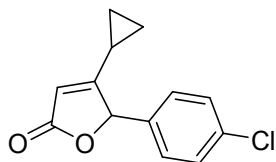
5-(4-Chlorophenyl)-4-(thiophen-2-yl)furan-2(5H)-one (3q).¹ Yellow solid, mp 120-121 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 (m, 1H), 7.50-7.44 (m, 4H), 7.39 (m, 1H), 7.12 (m, 1H), 6.71 (d, *J* = 1.5 Hz, 1H), 6.64 (d, *J* = 1.5 Hz, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 172.6, 159.9, 135.1, 134.8, 132.6 (2C), 131.6, 130.3, 129.7, 129.1, 112.3, 82.4; HRMS (EI) for C₁₇H₉ClO₂S (M⁺): calcd. 276.0012, found 276.0013.



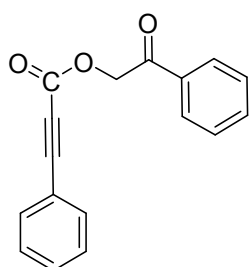
5-(4-Chlorophenyl)-4-(naphthalen-2-yl)furan-2(5H)-one (3r). Yellow solid, mp 178-179 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.85-7.80 (m, 2H), 7.78-7.74 (m, 2H), 7.53 (m, 3H), 7.32 (s, 4H), 6.67 (d, *J* = 1.5 Hz, 1H), 6.44 (d, *J* = 1.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 165.4, 135.7, 134.3, 133.7, 132.7, 129.5, 129.3, 129.1, 128.8, 128.2 (2C), 127.8, 127.2, 126.8, 123.9, 115.4, 83.4; HRMS (EI) for C₁₇H₉ClO₂S (M⁺): calcd. 320.0604, found 320.0608.



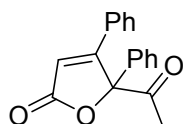
4-(tert-Butyl)-5-(4-chlorophenyl)furan-2(5H)-one (3s). Yellow oil; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.27 (d, *J* = 1.6 Hz, 1H), 6.20 (d, *J* = 1.6 Hz, 1H), 0.95 (s, 9H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 180.9, 173.1, 135.1, 134.4, 130.1 (2C), 129.4, 115.3, 83.5, 34.1, 29.7; HRMS (EI) for C₁₄H₁₅ClO₂ (M⁺): calcd. 250.0761, found 250.0762.



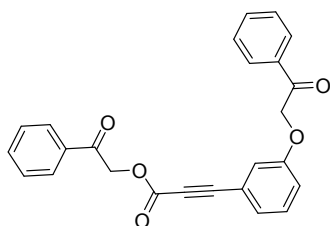
5-(4-Chlorophenyl)-4-cyclopropylfuran-2(5H)-one (3t). Yellow oil; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.51-7.47 (m, 2H), 7.37-7.33 (m, 2H), 6.18 (s, 1H), 5.88 (d, $J = 1.0$ Hz, 1H), 1.39-1.32 (m, 1H), 1.02-0.88 (m, 2H), 0.78-0.66 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 177.6, 173.5, 134.7, 134.4, 129.5 (2C), 110.0, 84.1, 12.2, 11.6, 10.2; HRMS (EI) for $\text{C}_{13}\text{H}_{11}\text{ClO}_2$ (M^+): calcd. 234.0448, found 234.0446.



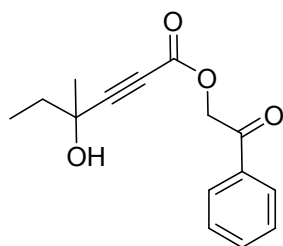
2-Oxo-2-phenylethyl 3-phenylpropiolate (4a).² White solid; mp 89-90 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.8$ Hz, 2H), 7.63 (t, $J = 6.8$ Hz, 3H), 7.53-7.44 (m, 3H), 7.39 (t, $J = 7.6$ Hz, 2H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.9, 153.2, 134.0 (2C), 133.1, 130.8, 128.9, 128.3, 127.8, 119.3, 87.9, 79.9, 67.0; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{NaO}_3$ [$\text{M}+\text{Na}$] $^+$ 287.0684, found 287.0678.



5-Acetyl-4,5-diphenylfuran-2(5H)-one (5v).¹ Colorless oil; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.60 – 7.57 (m, 2H), 7.47 – 7.36 (m, 8H), 7.28 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 203.6, 171.5, 164.2, 136.0, 131.9, 130.0, 129.7, 129.4, 129.1, 128.4(2C), 117.9, 95.7, 26.5; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{NaO}_3$ [$\text{M}+\text{H}$] $^+$ 279.1021, found 279.1034.



2-oxo-2-phenylethyl 3-(3-(2-oxo-2-phenylethoxy)phenyl)propiolate (4w). White solid; mp 181-182 °C; ¹H NMR (400 MHz, DMSO) δ 8.07 – 8.02 (m, 2H), 8.01 – 7.96 (m, 2H), 7.73 – 7.68 (m, 2H), 7.57 (m, 4H), 7.45 – 7.38 (m, 2H), 7.33 – 7.30 (m, 1H), 7.23 (m, 1H), 5.71 (d, *J* = 6.9 Hz, 4H); ¹³C NMR (100 MHz, DMSO) δ 194.6, 192.0, 158.5, 153.0, 134.8, 134.7, 134.3, 134.1, 130.8, 129.5, 129.3, 128.4, 128.3, 126.2, 119.6 (2C), 118.4, 87.3, 80.3, 70.8, 68.5; HRMS (ESI) calcd for C₂₅H₁₇O₅ [M-H]⁻ 397.1073, found 397.1071.

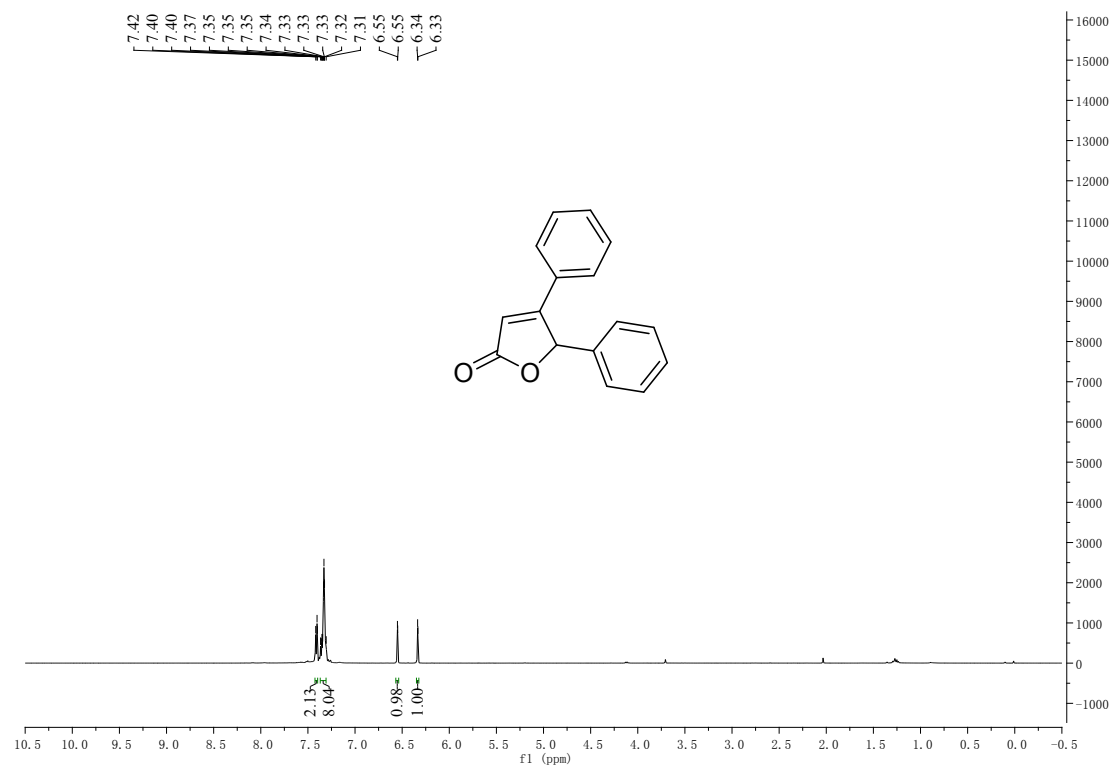


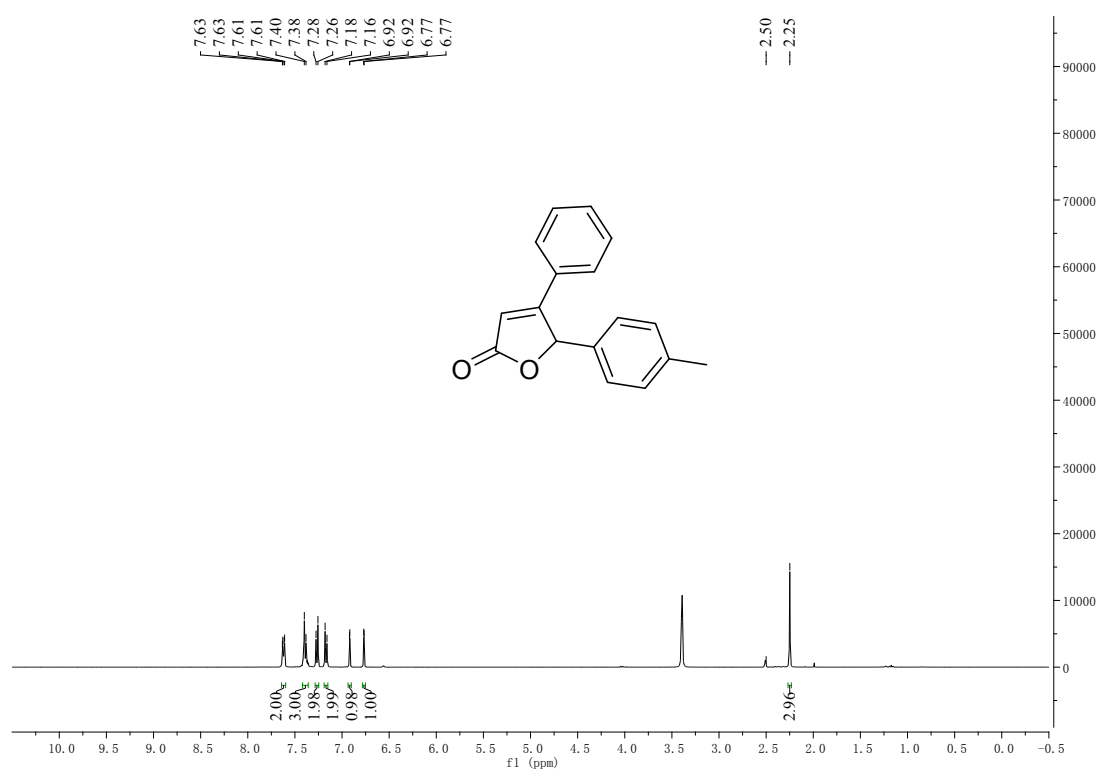
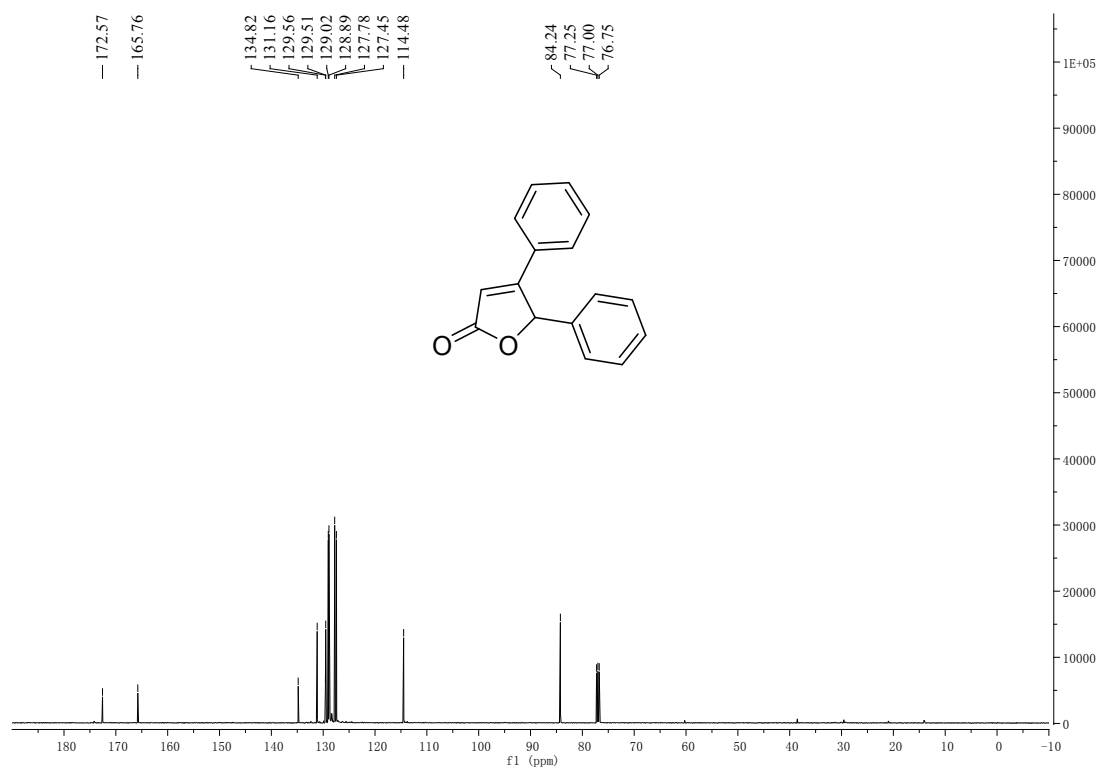
2-oxo-2-phenylethyl 4-hydroxy-4-methylhex-2-ynoate (4x). White solid; mp 141-143 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.41 (s, 2H), 2.58 (s, 1H), 1.77 (m, 2H), 1.53 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 190.9, 152.8, 134.0, 133.9, 129.0, 127.8, 92.3, 74.5, 68.6, 67.0, 35.9, 28.3, 8.7; HRMS (ESI) calcd for C₁₅H₁₅O₄ [M-H]⁻ 259.0971, found 259.0976.

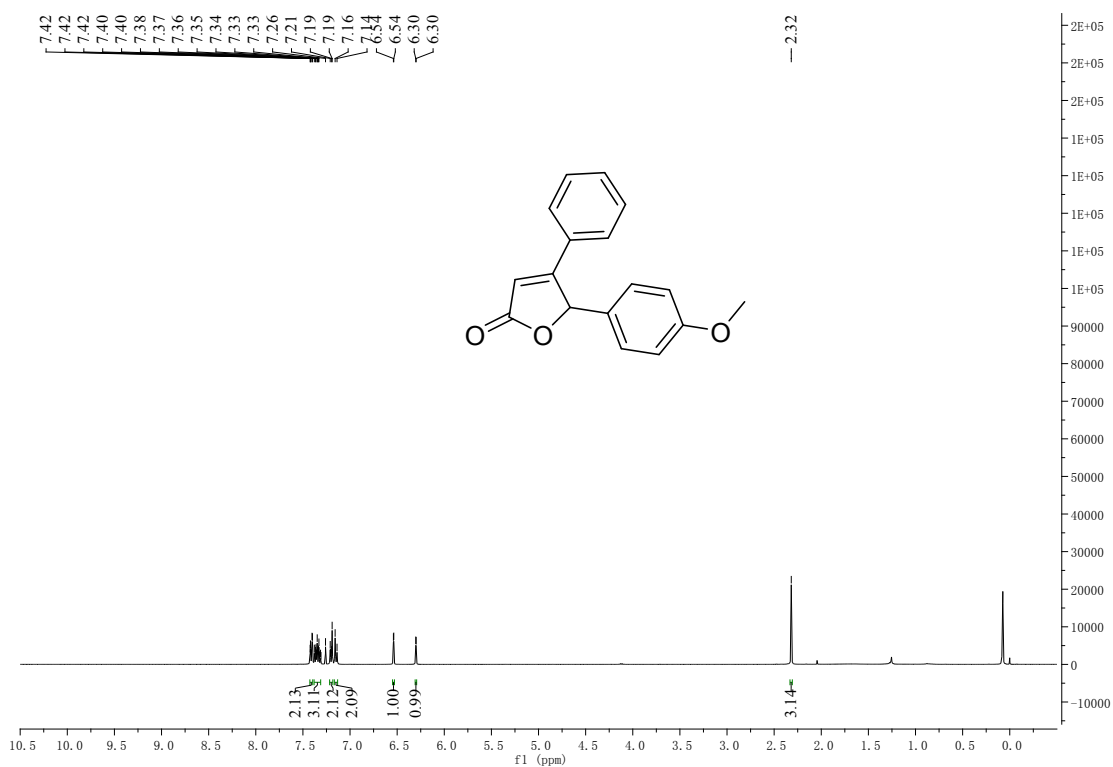
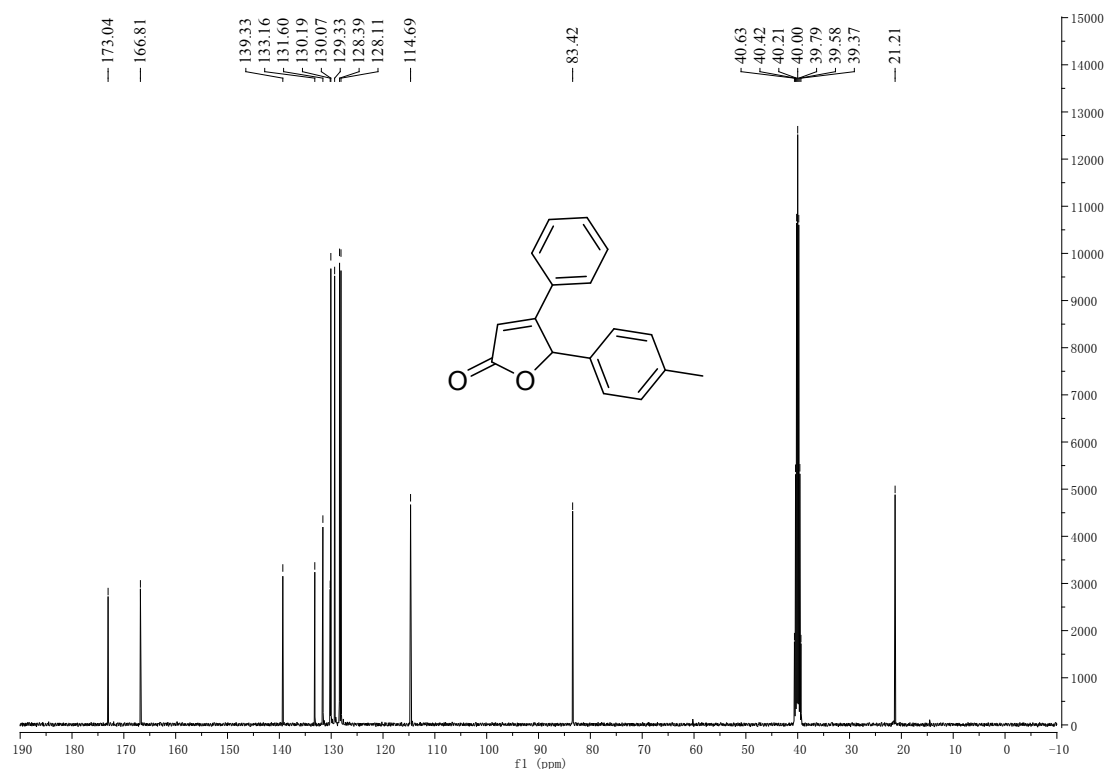
IV. References

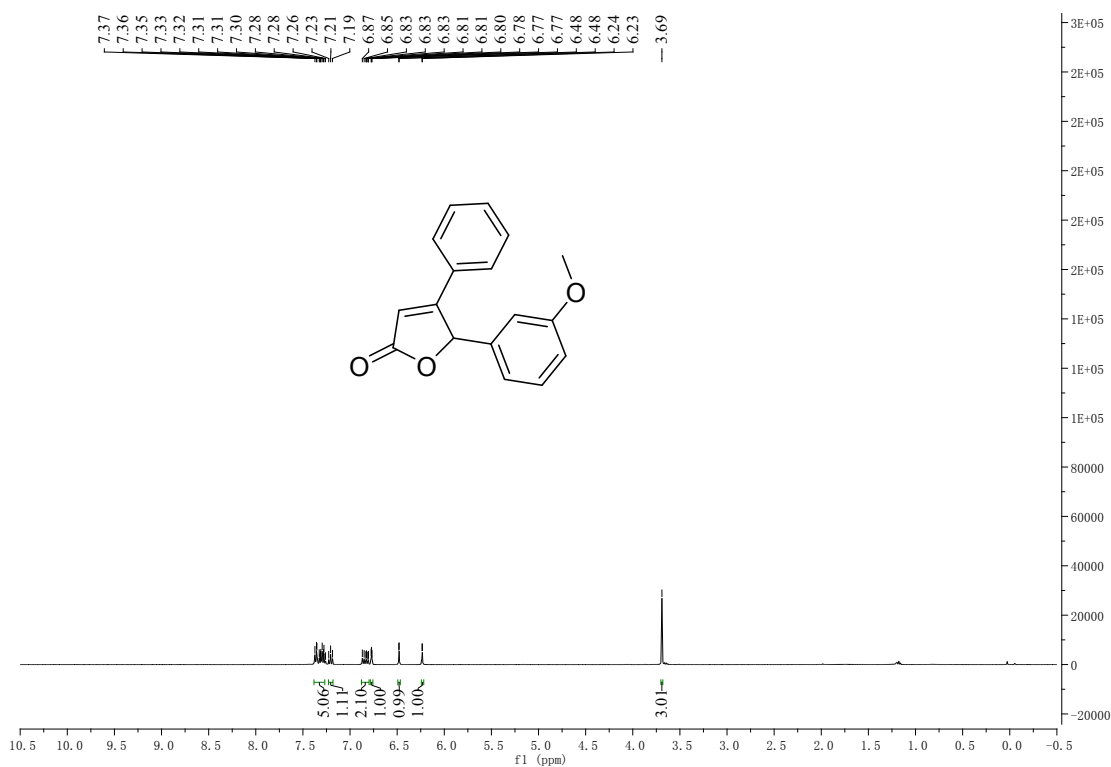
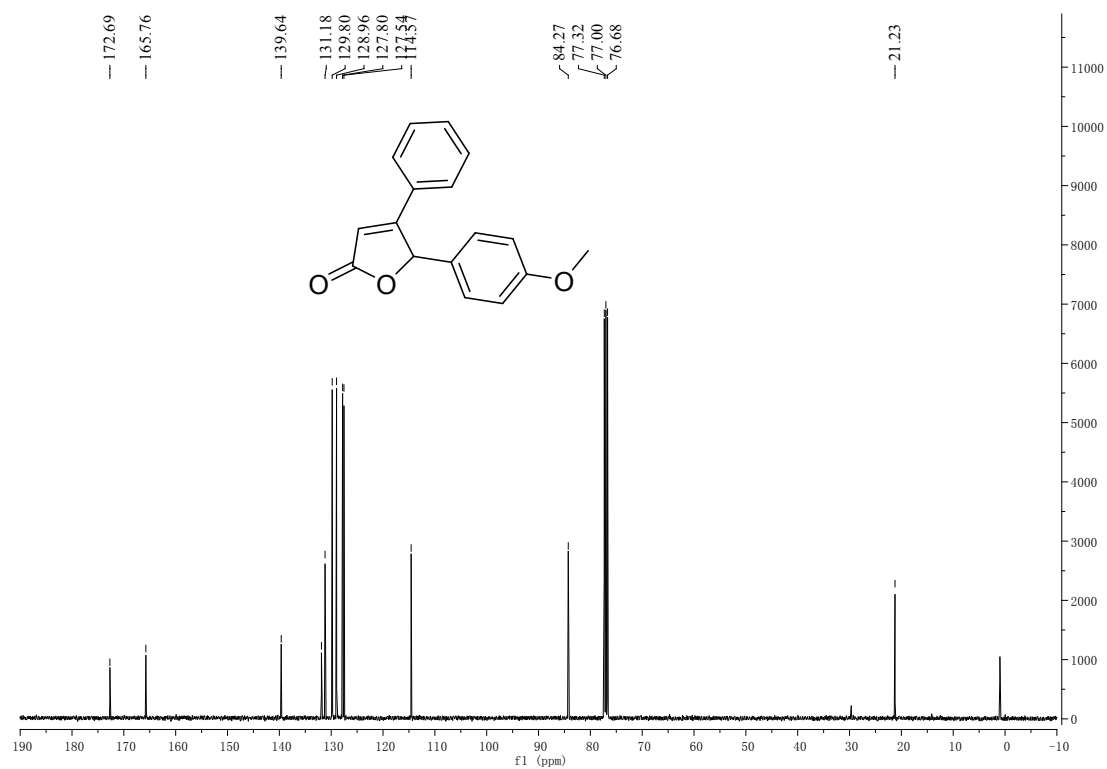
1. Y. Lei, Z. Q. Wang, Y. X. Xie, S. C. Yu, B. X. Tang, and J. H. Li, *Adv. Synth. Catal.* 2011, **353**, 31.
2. J. Song, Q. Shen, F. Xu, X. Lu, *Org. Lett.* 2007, **9**, 2947.
3. S. H. Kim, K. H. Kim, and S. H. Hong, *Angew. Chem.*, 2014, **126**, 790.
4. Y. Lei, Z. Q. Wang, Y. X. Xie, S. C. Yu, B. X. Tang, and J. H. Li, *Adv. Synth. Catal.*, 2011, **353**, 31.

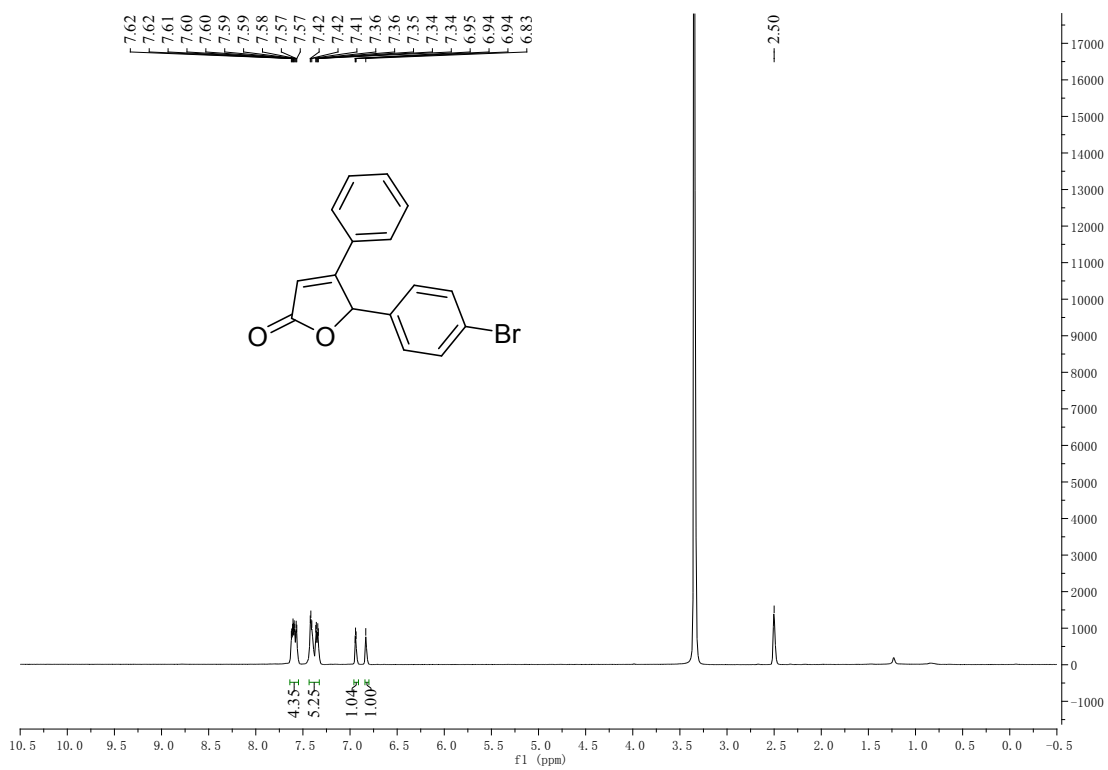
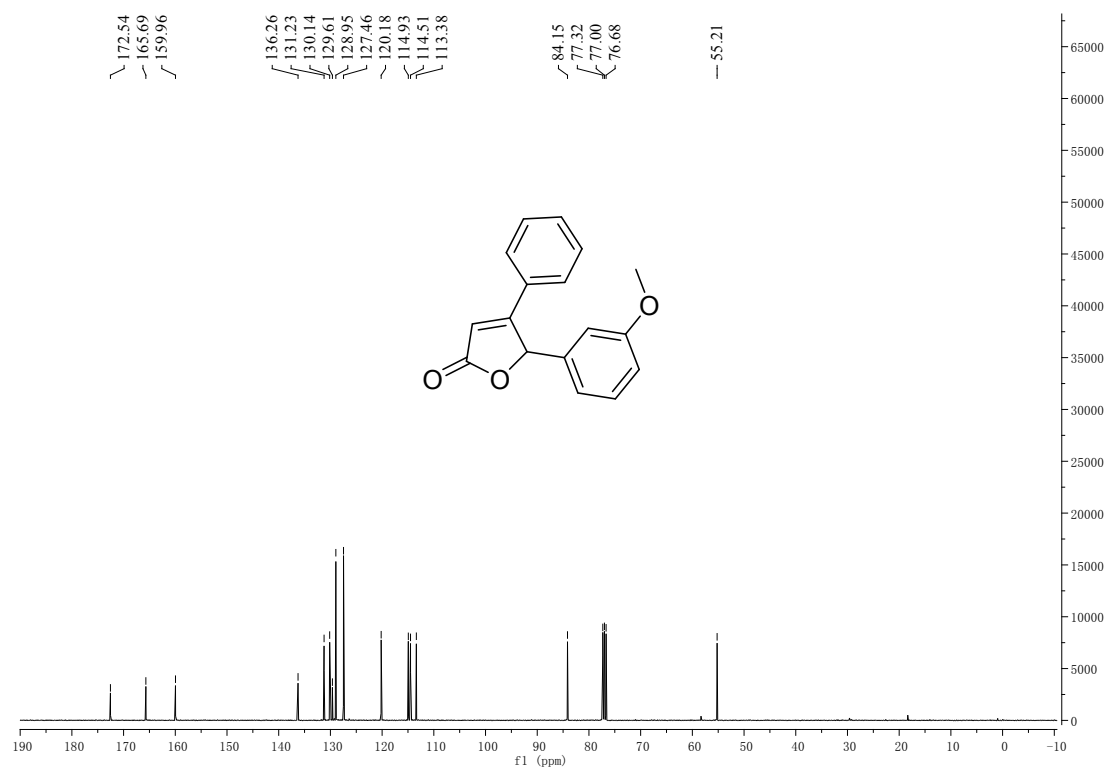
V. NMR Spectra for All Compounds

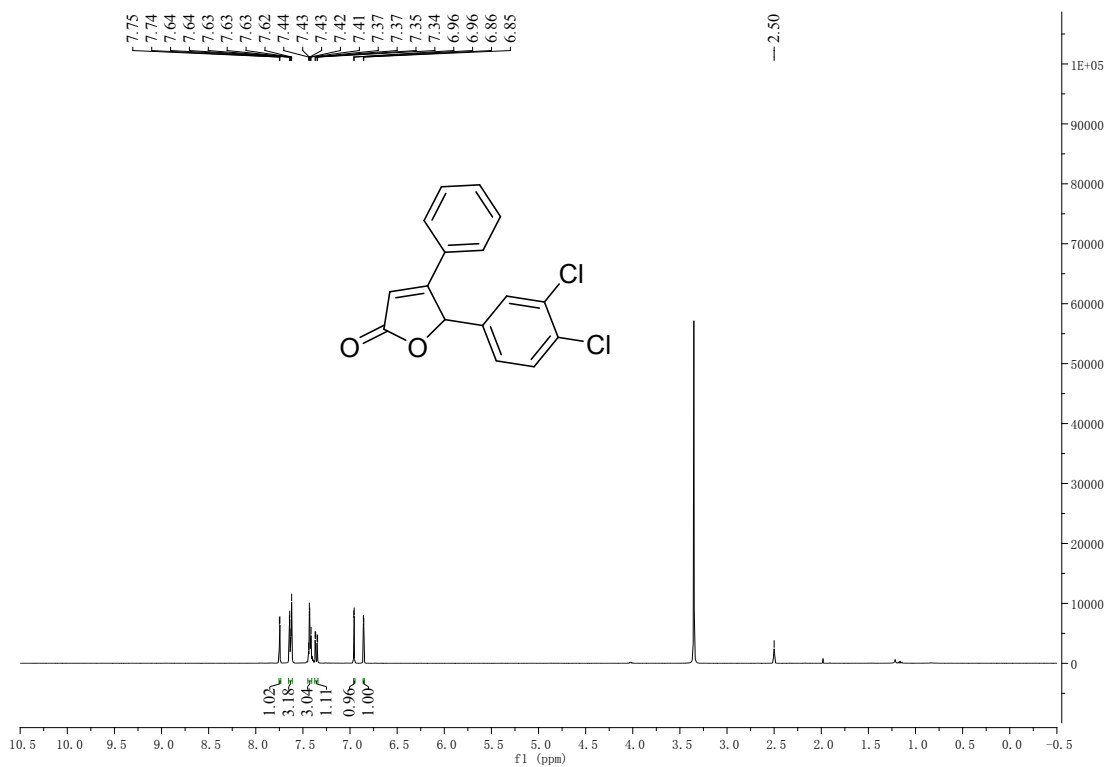
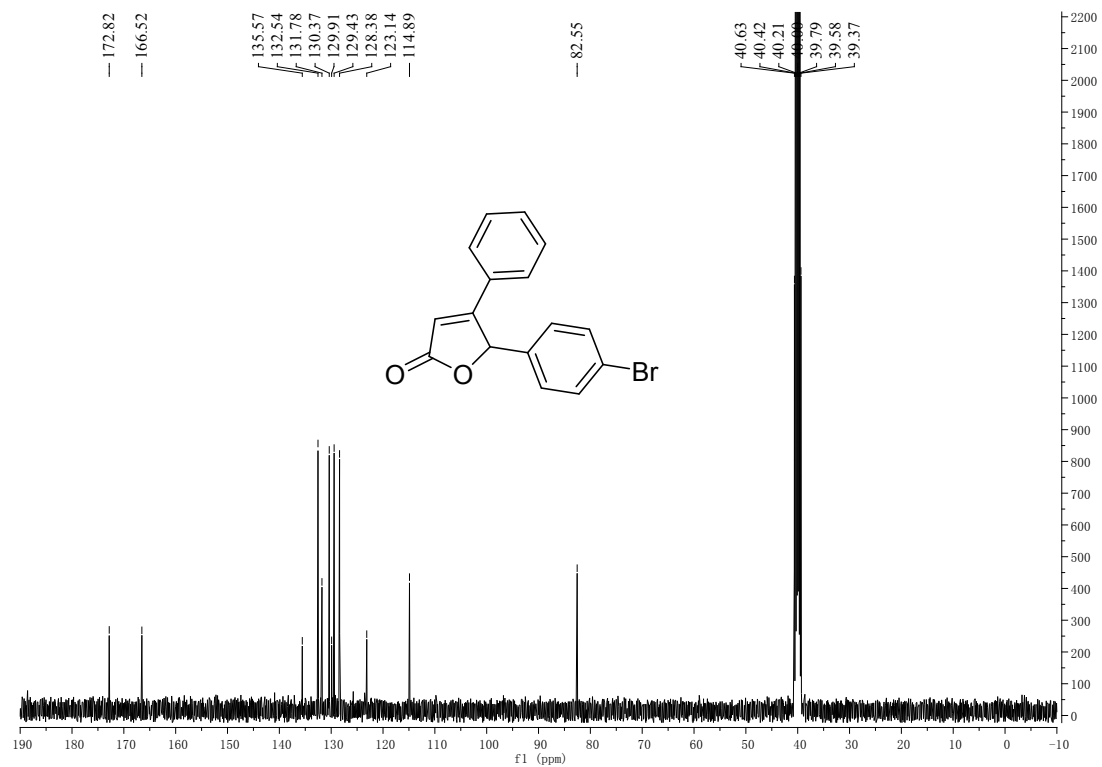


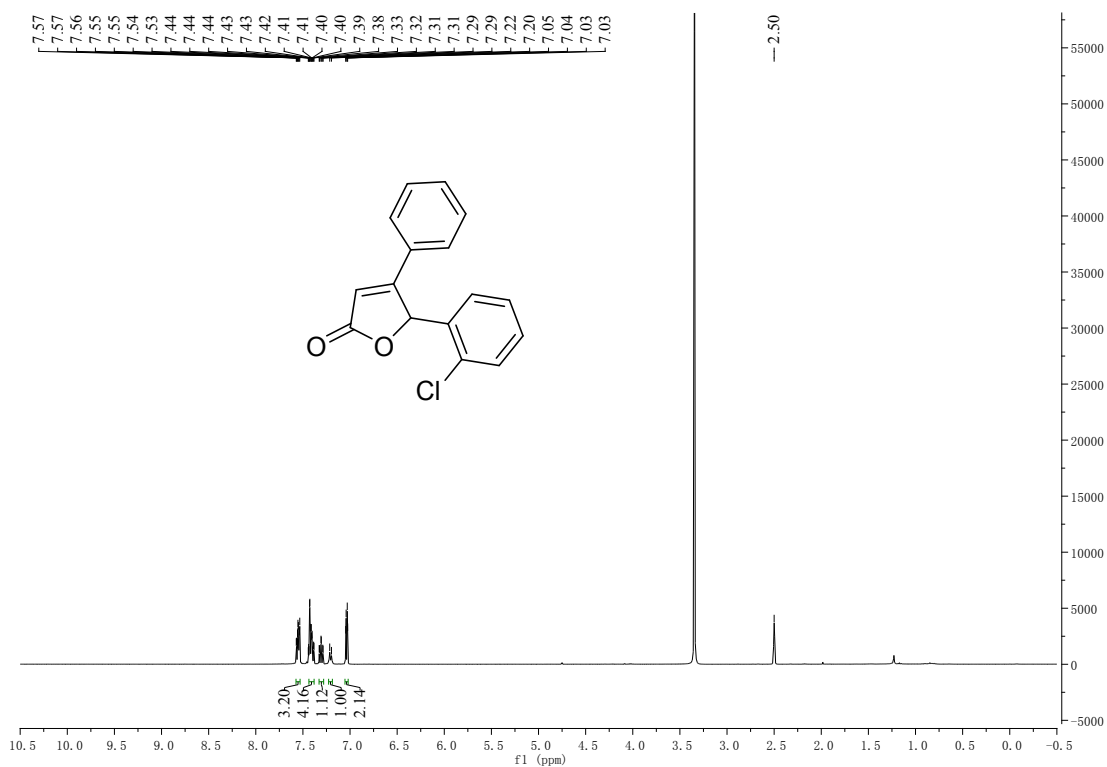
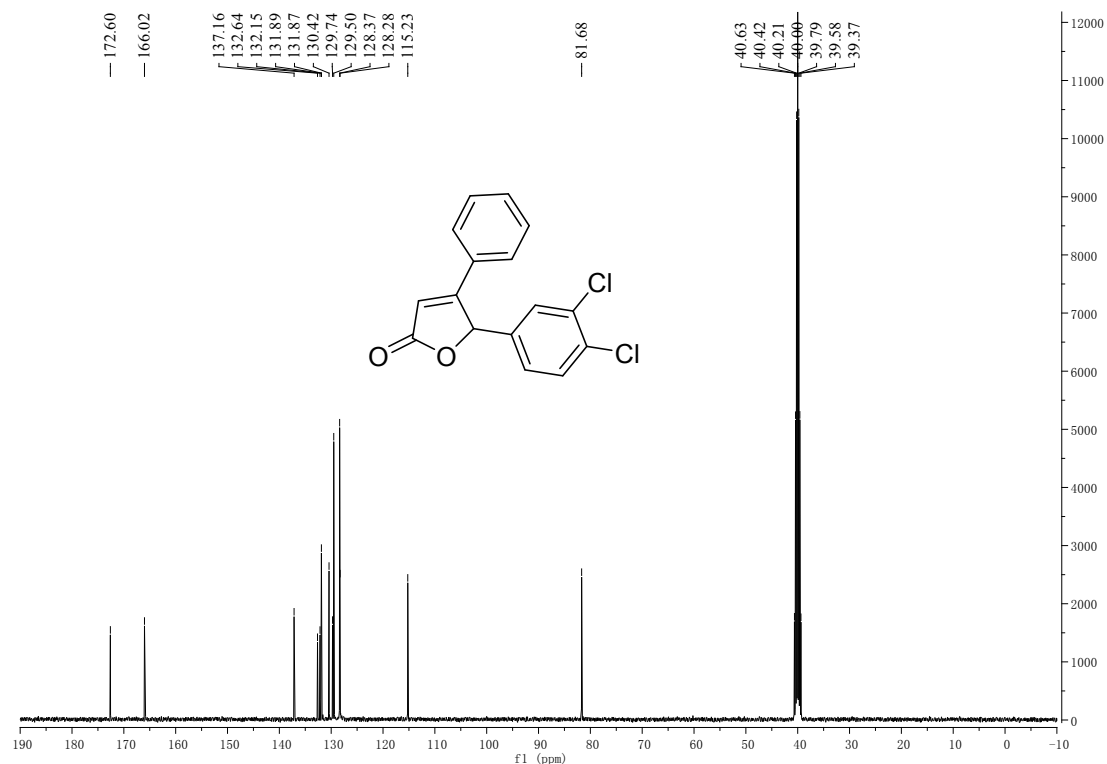


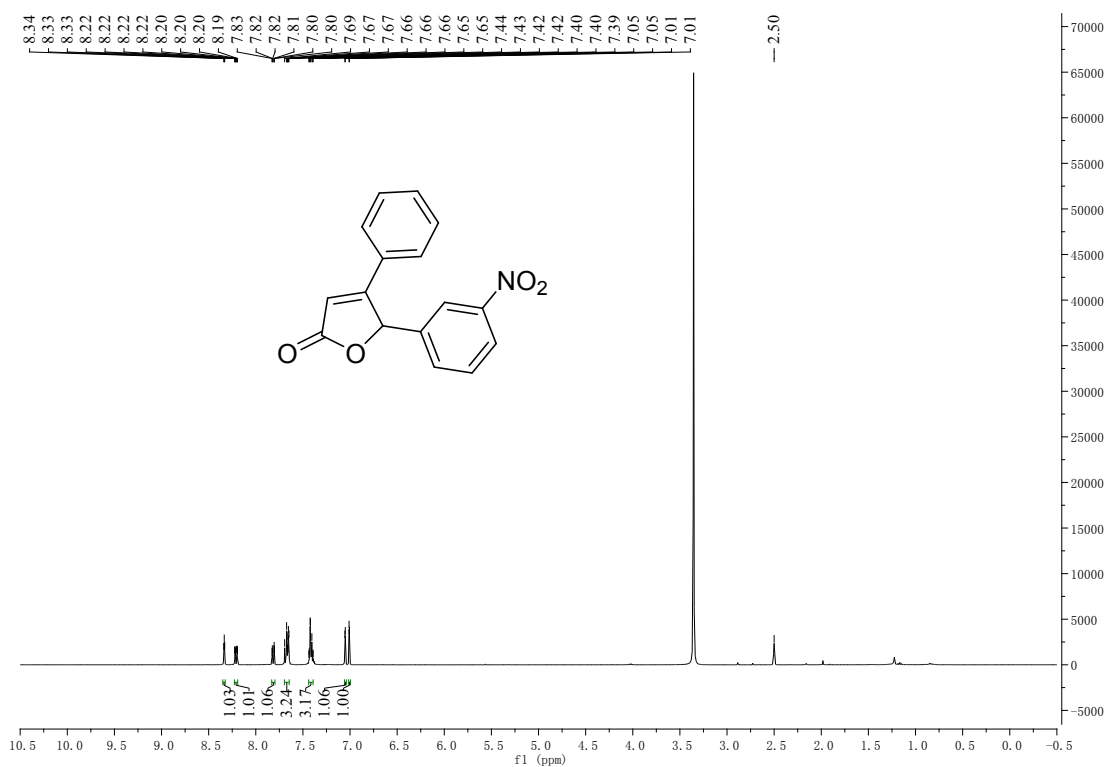
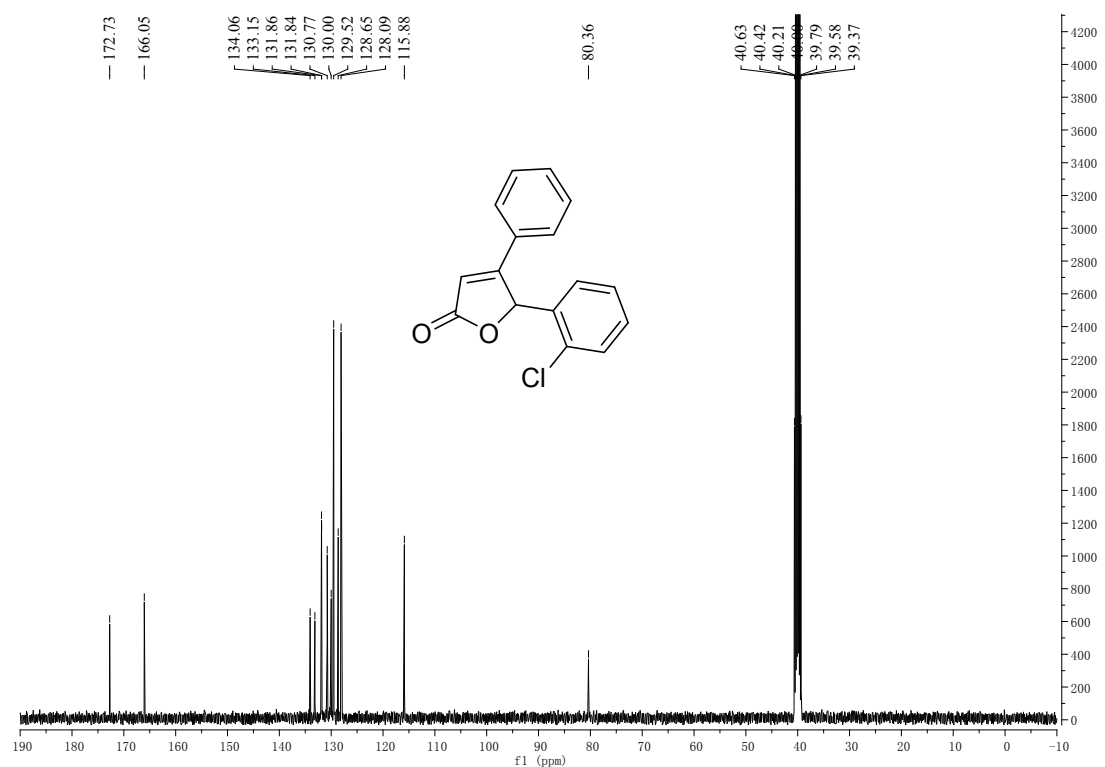


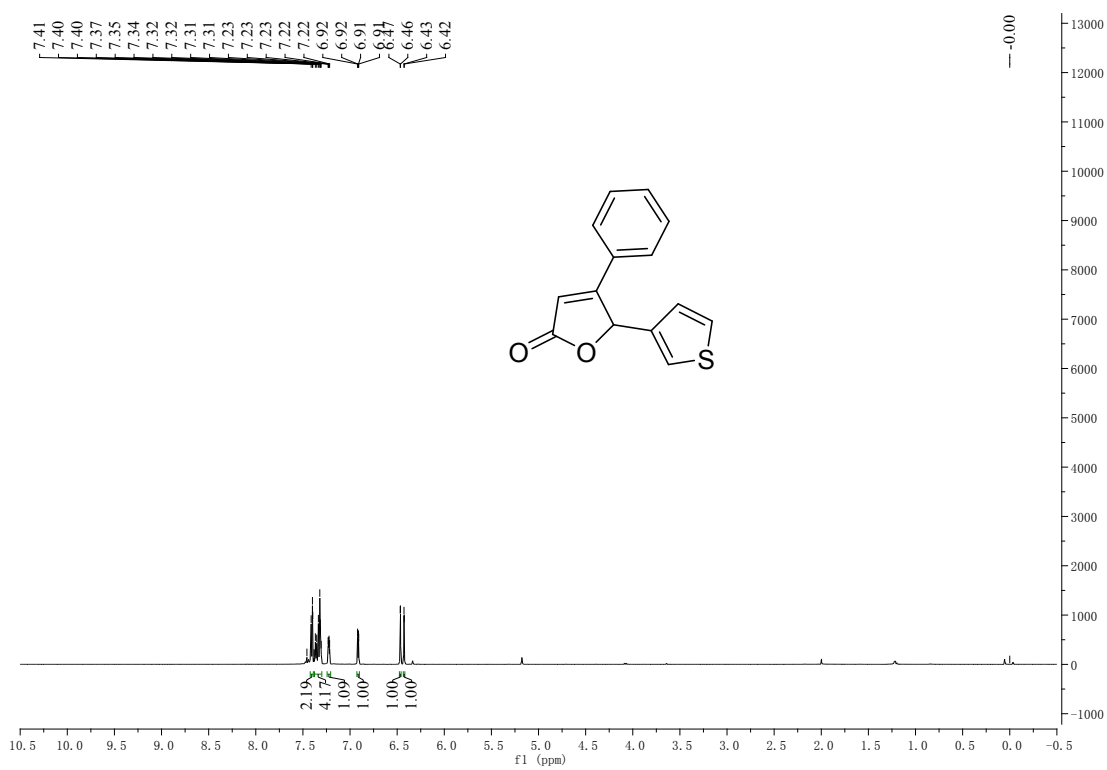
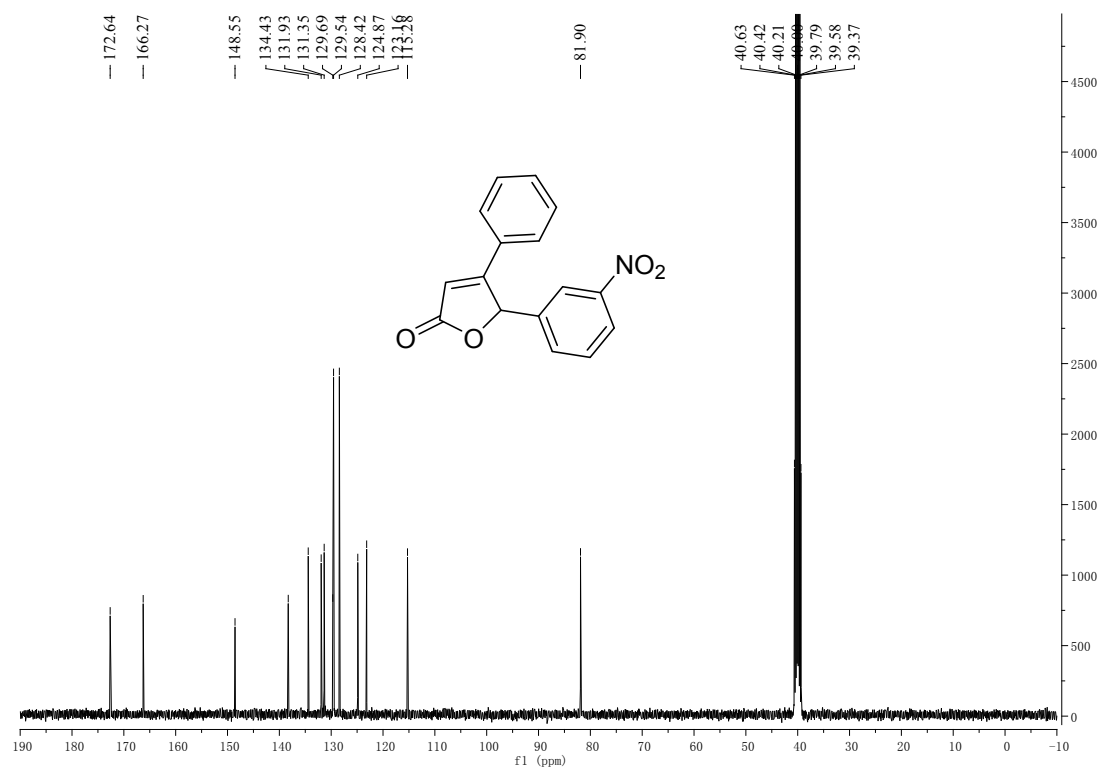


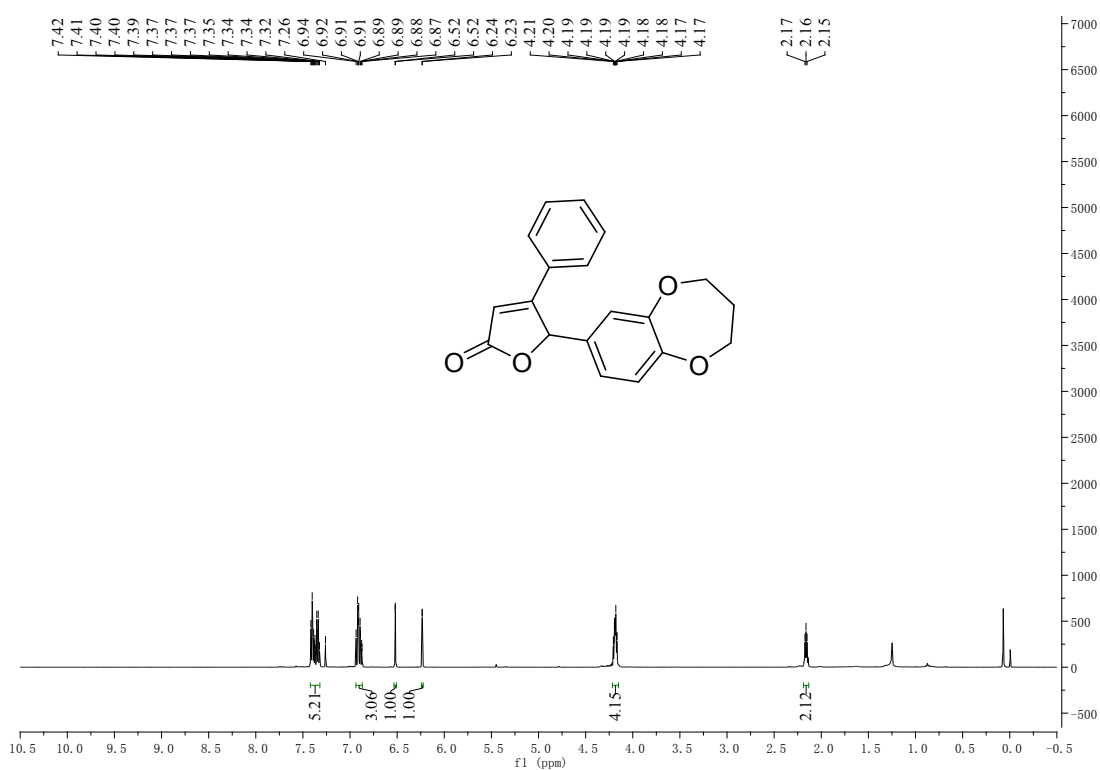
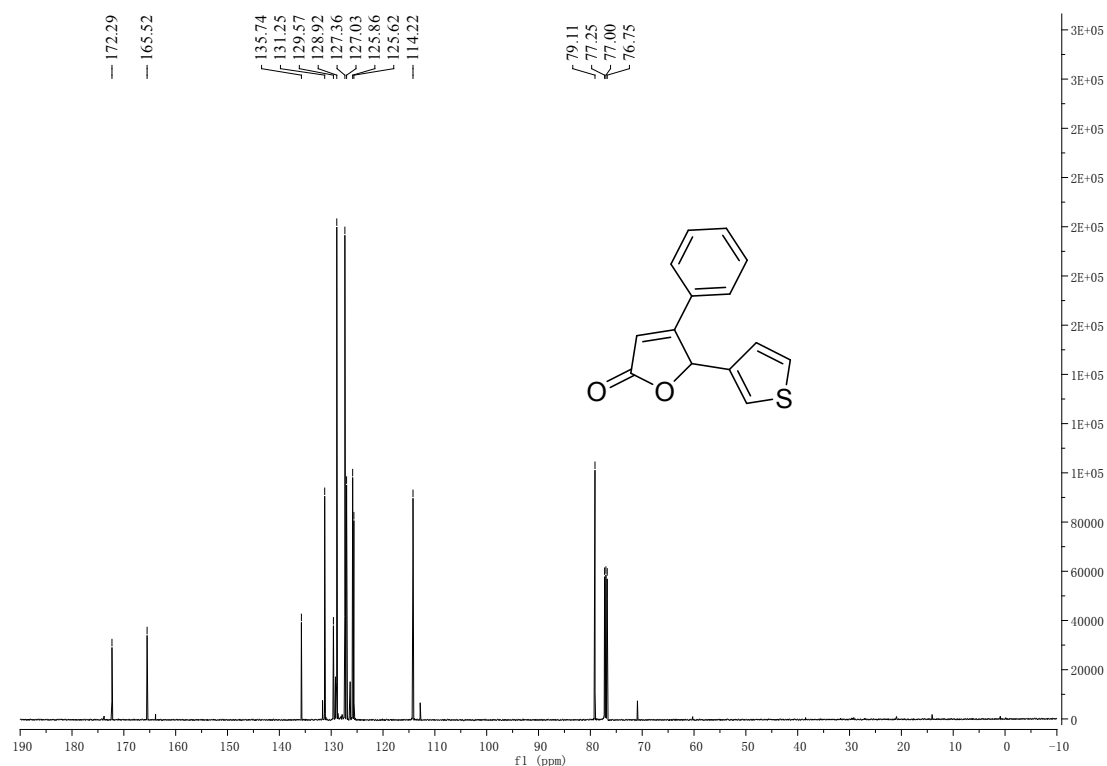


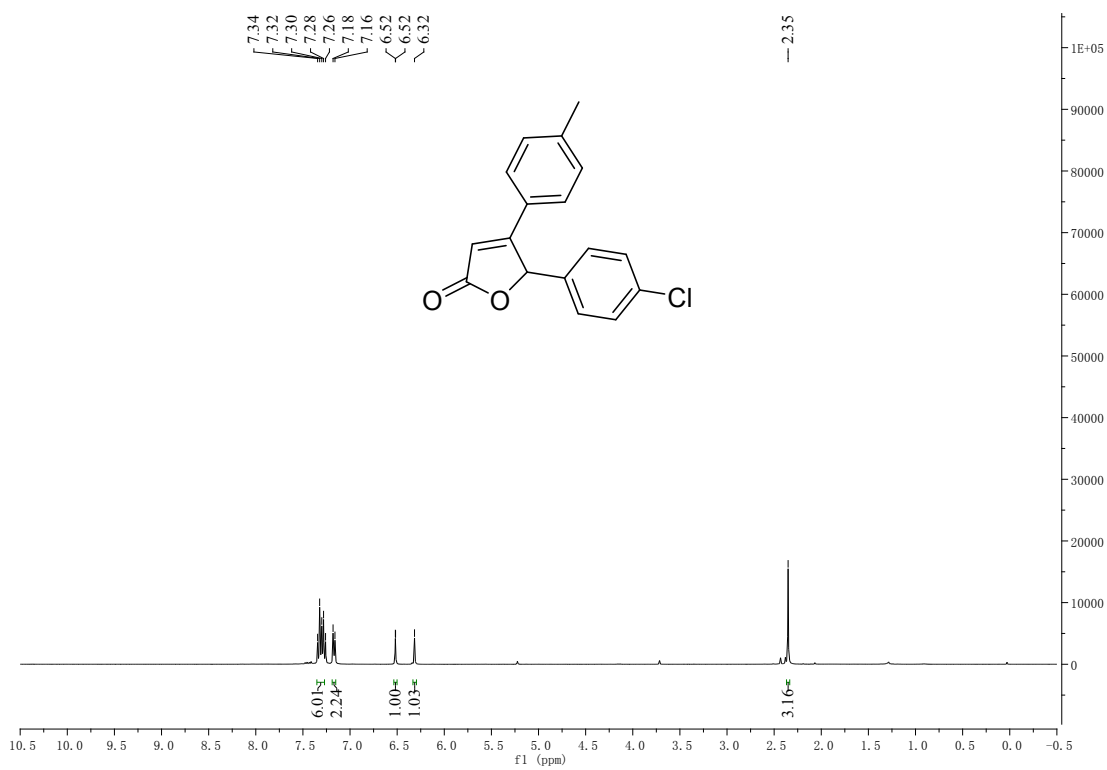
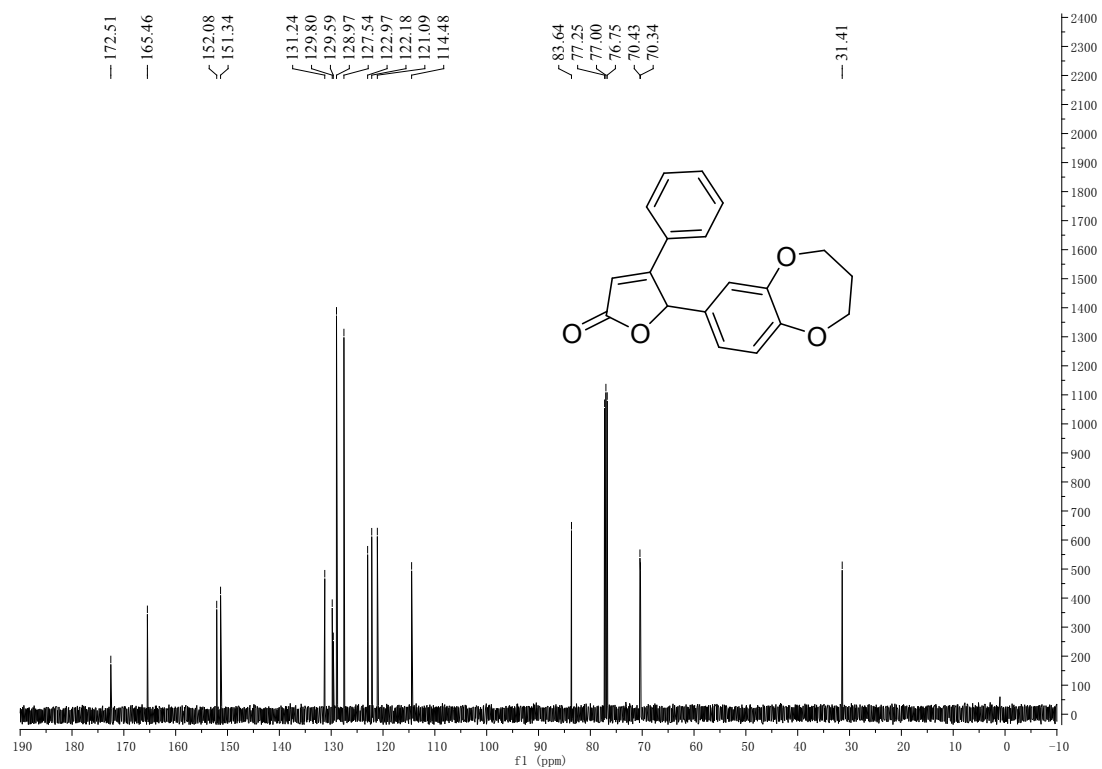


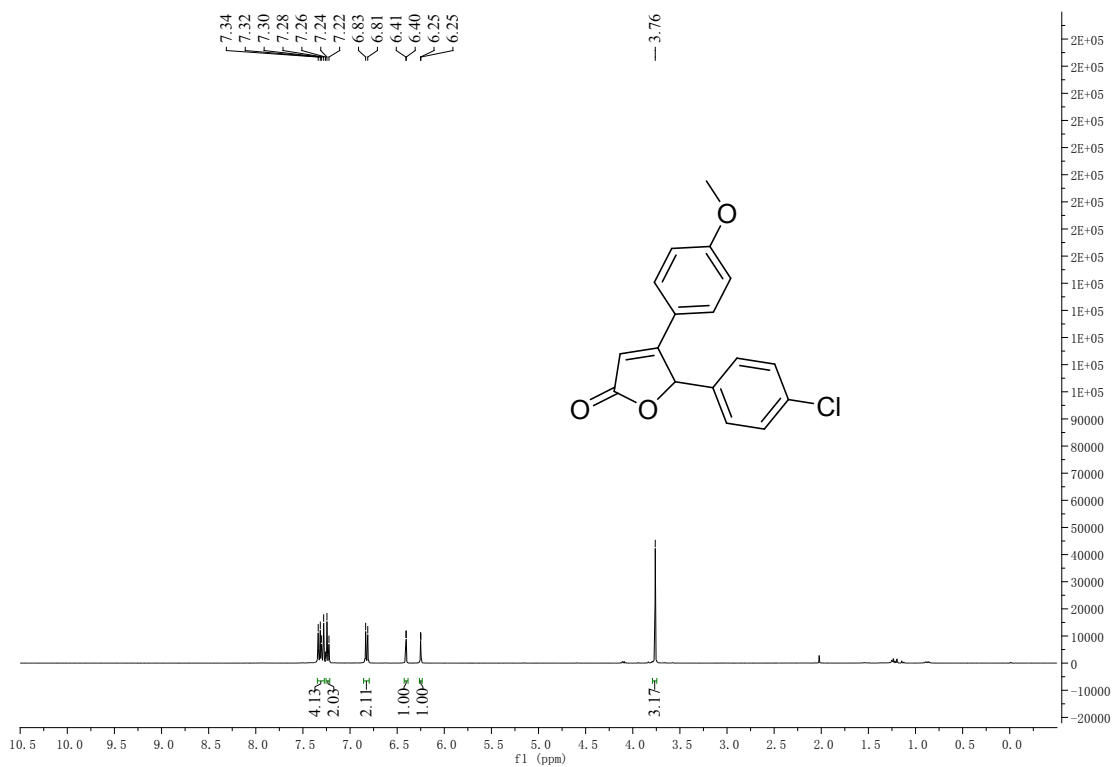
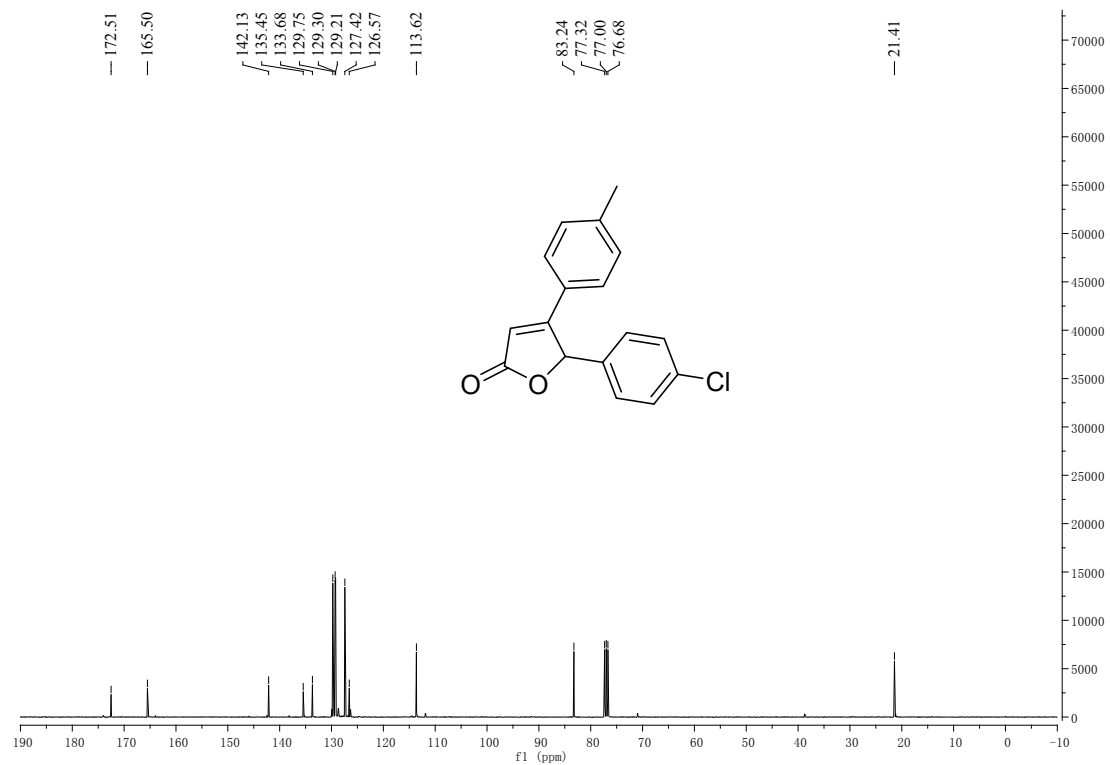


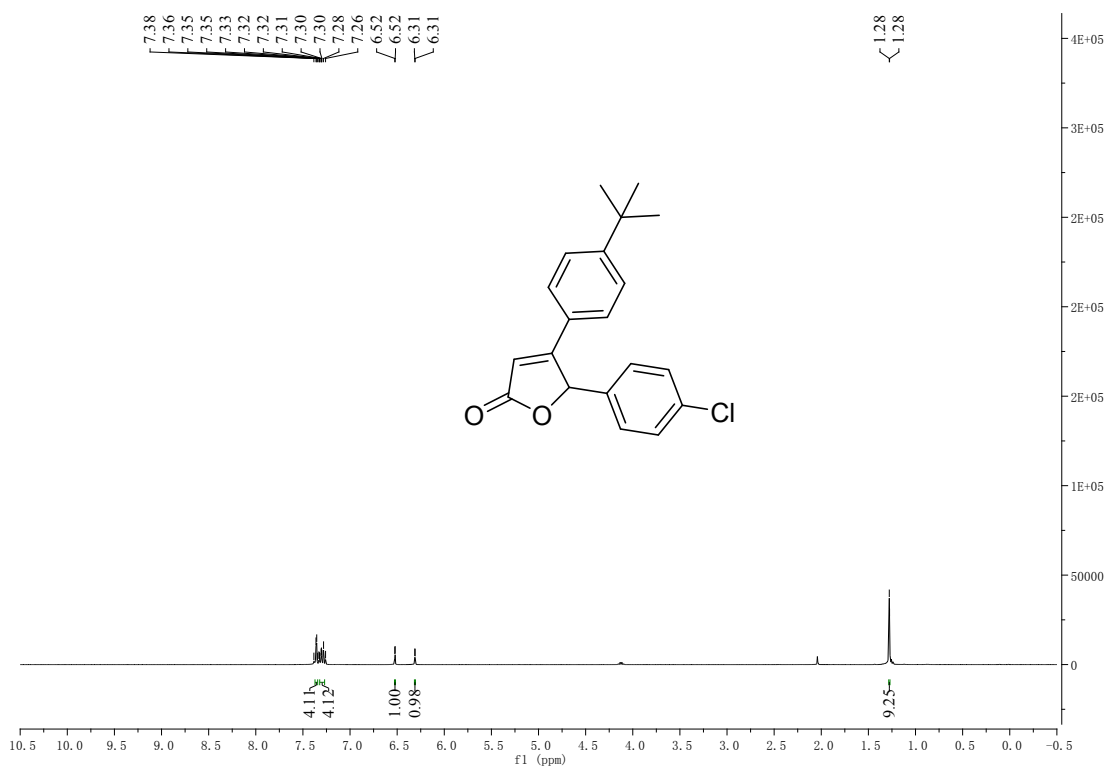
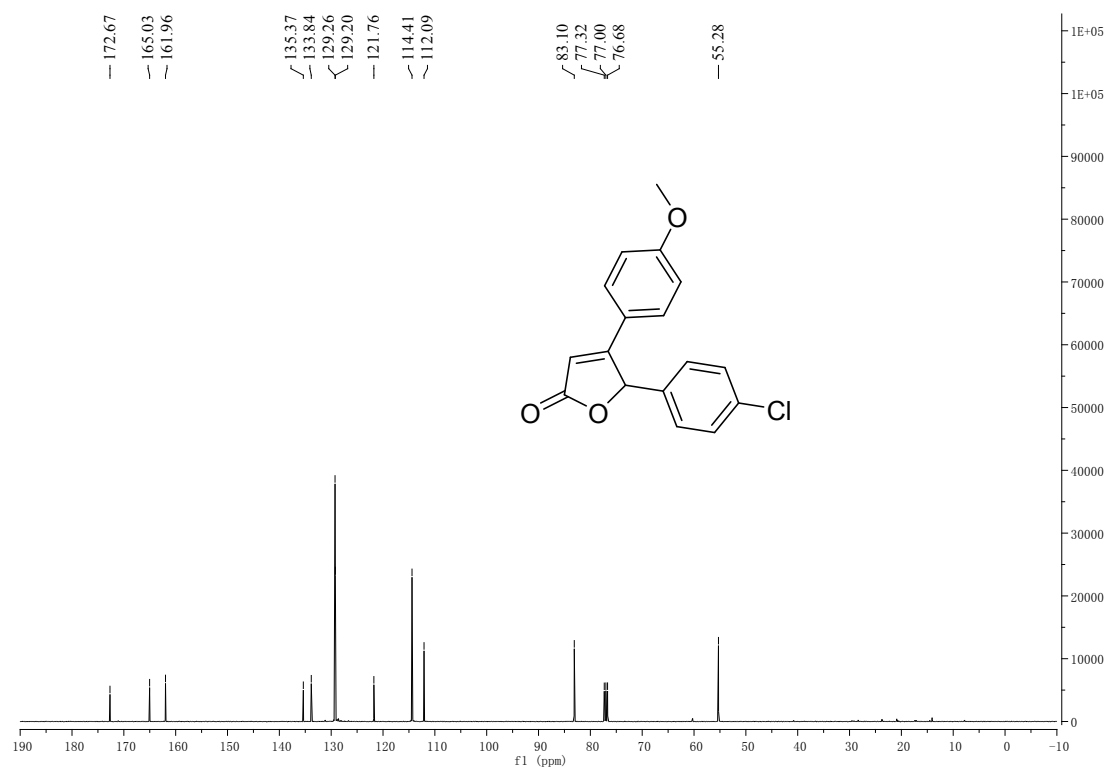


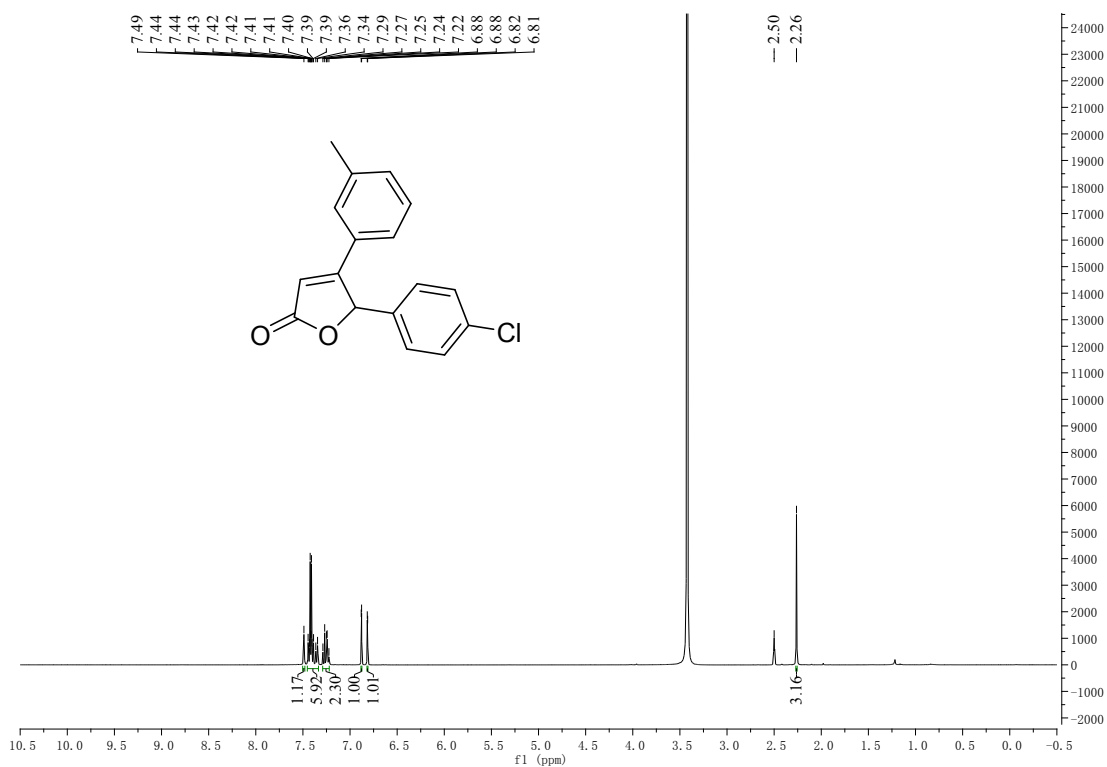
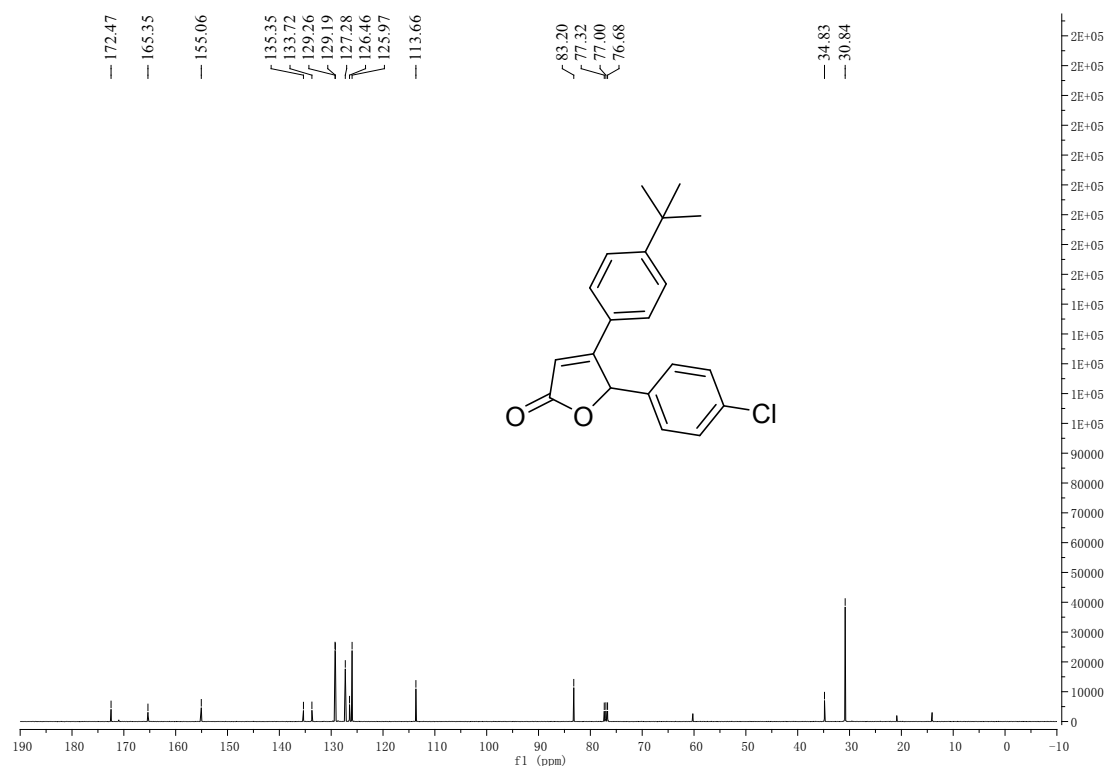


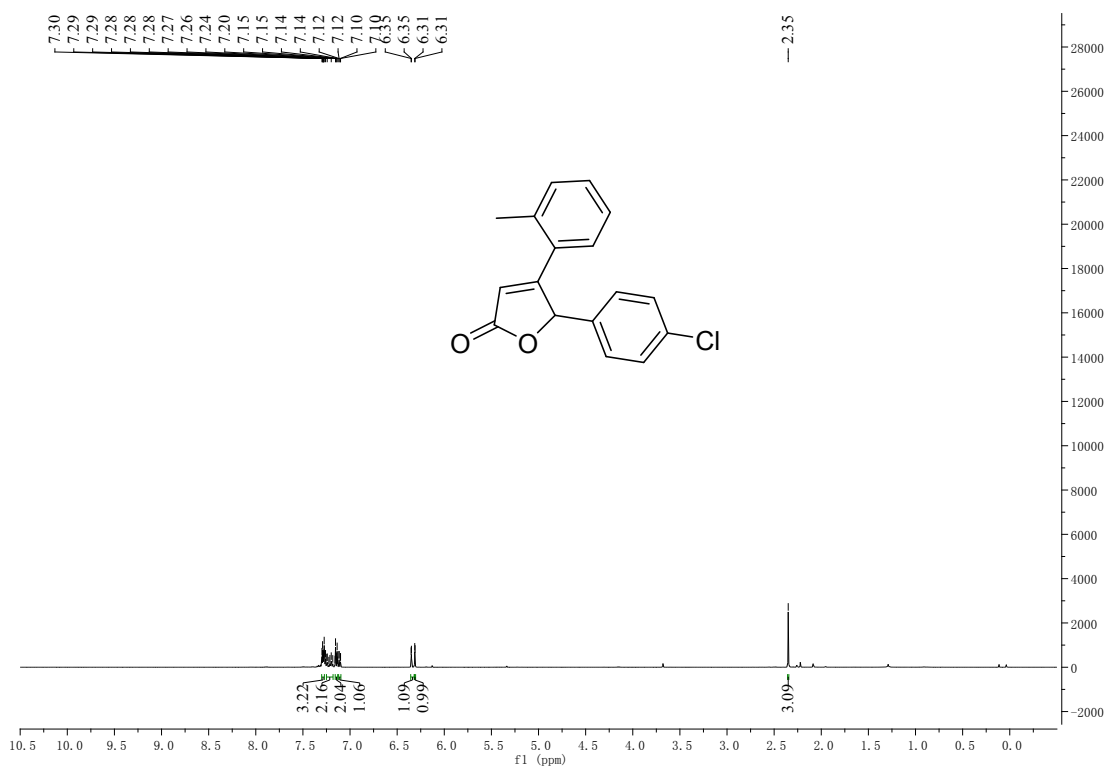
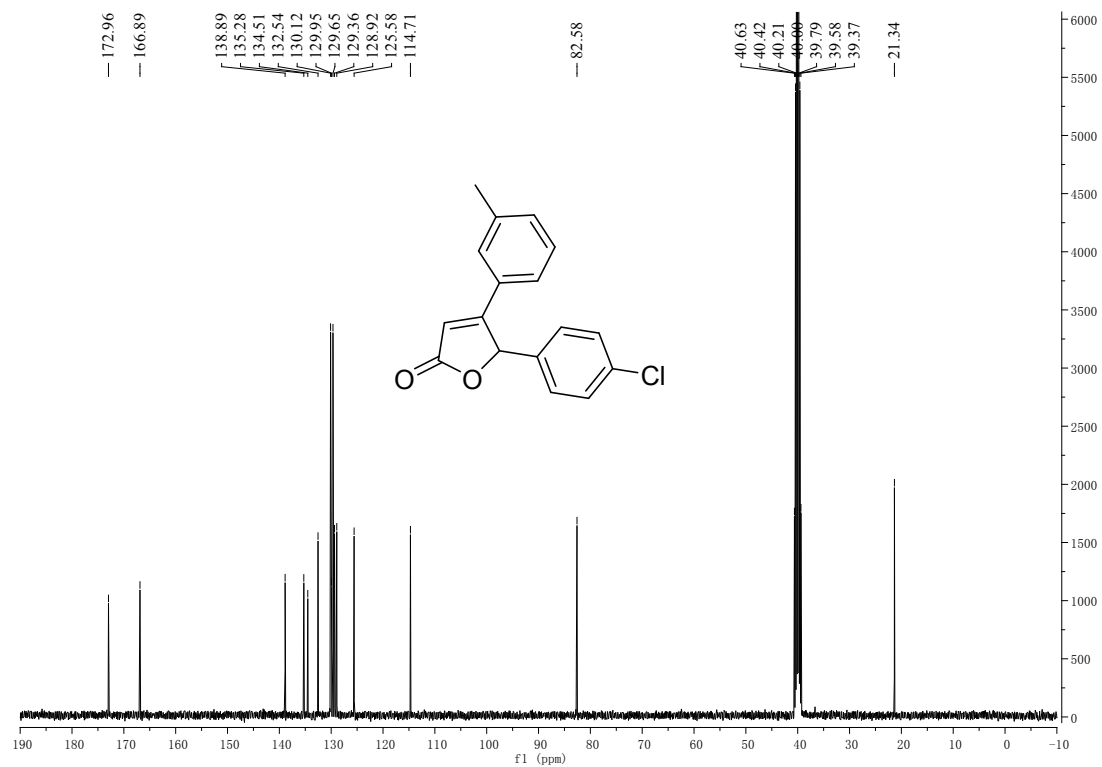


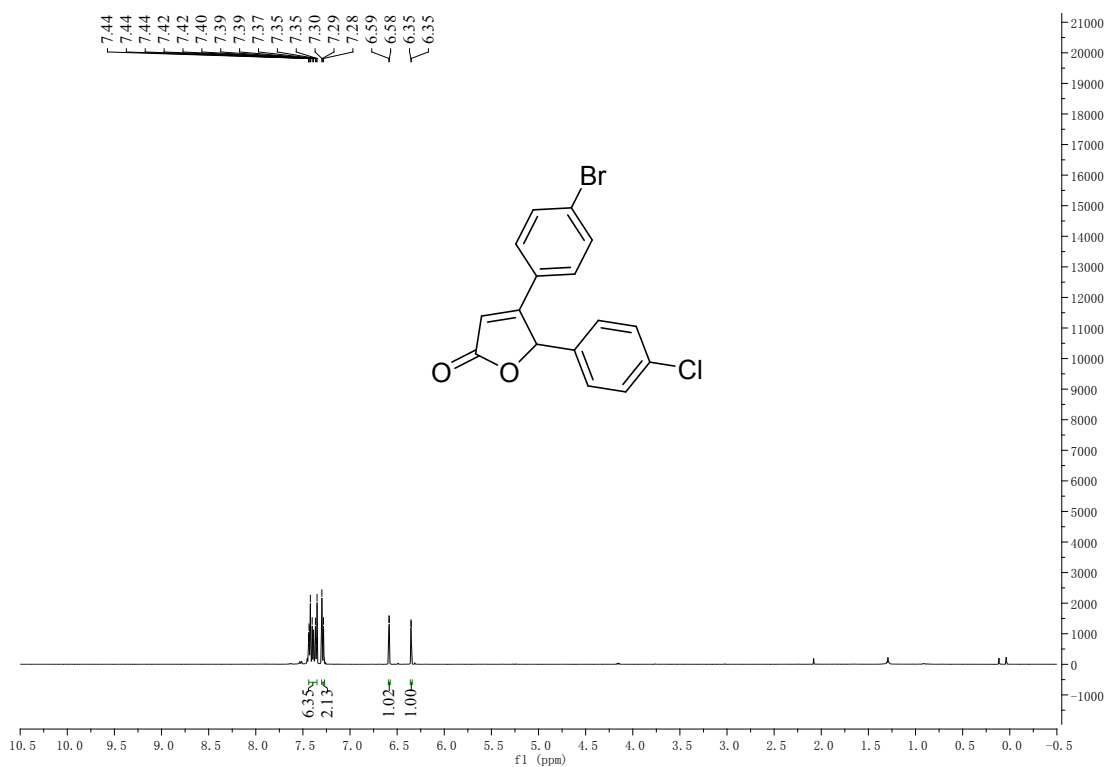
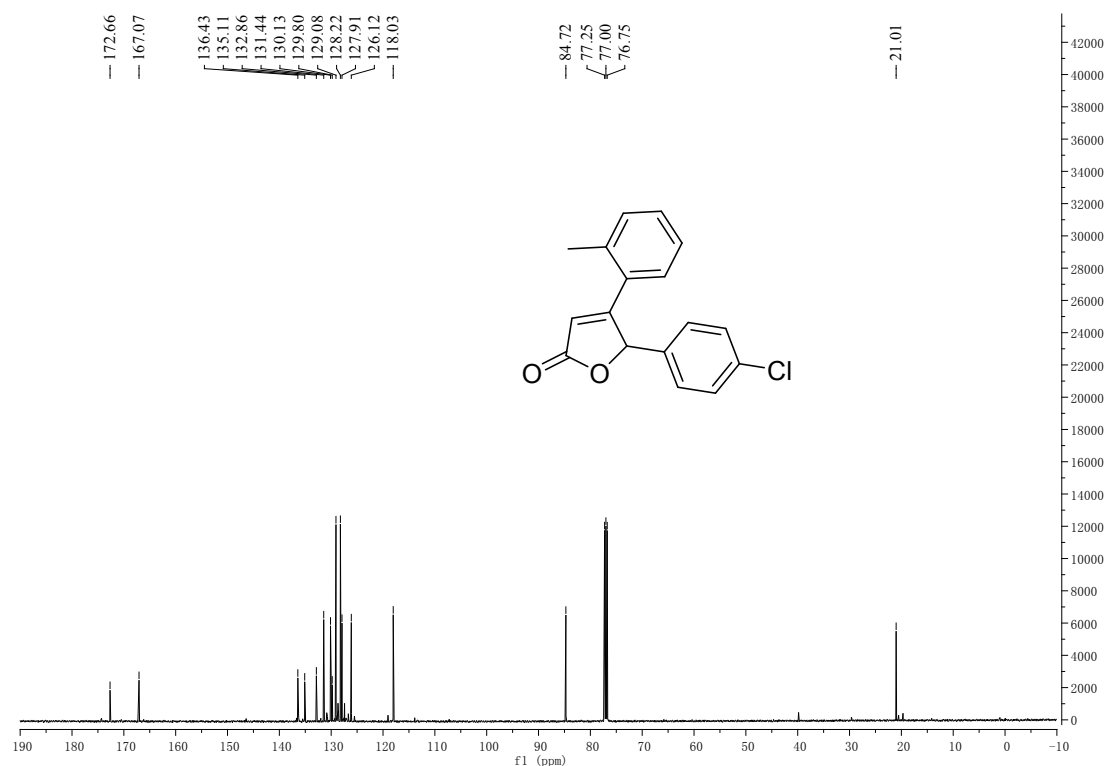


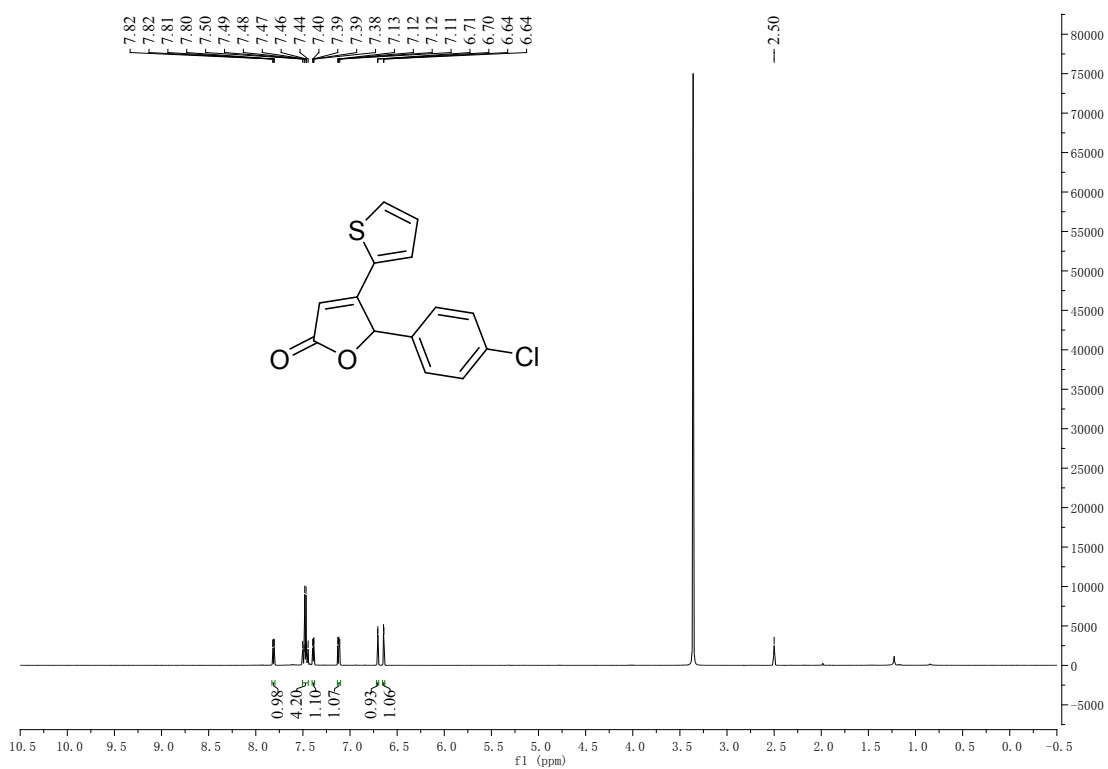
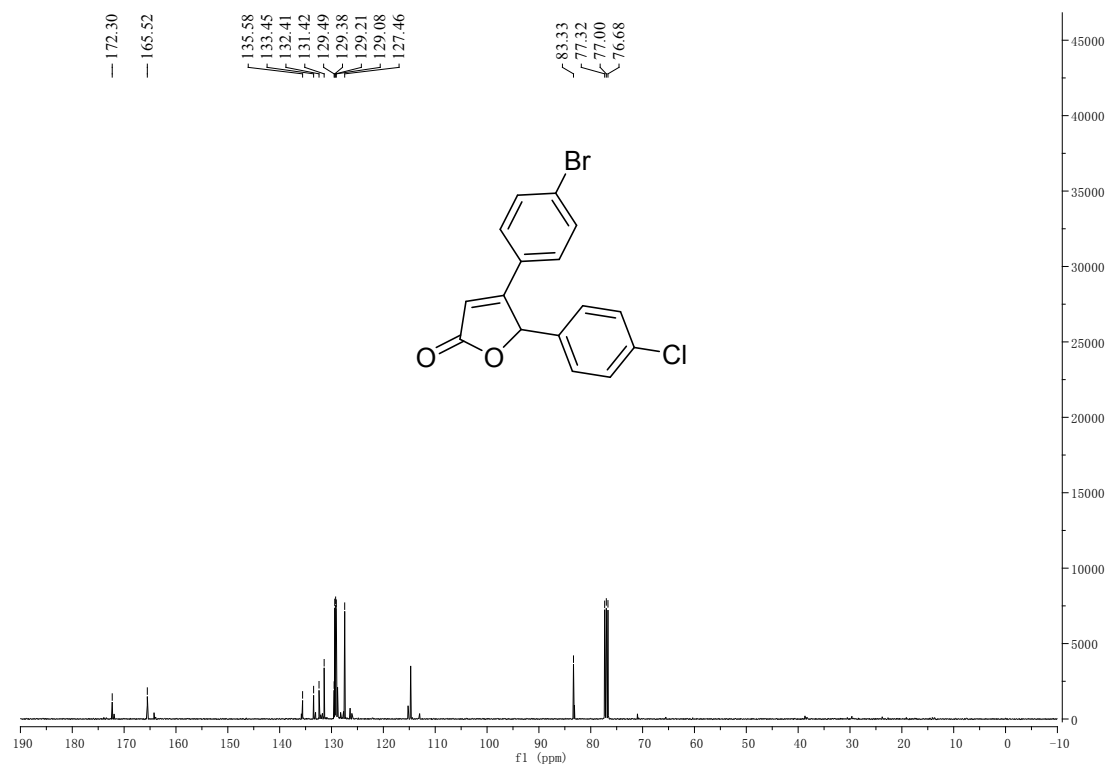


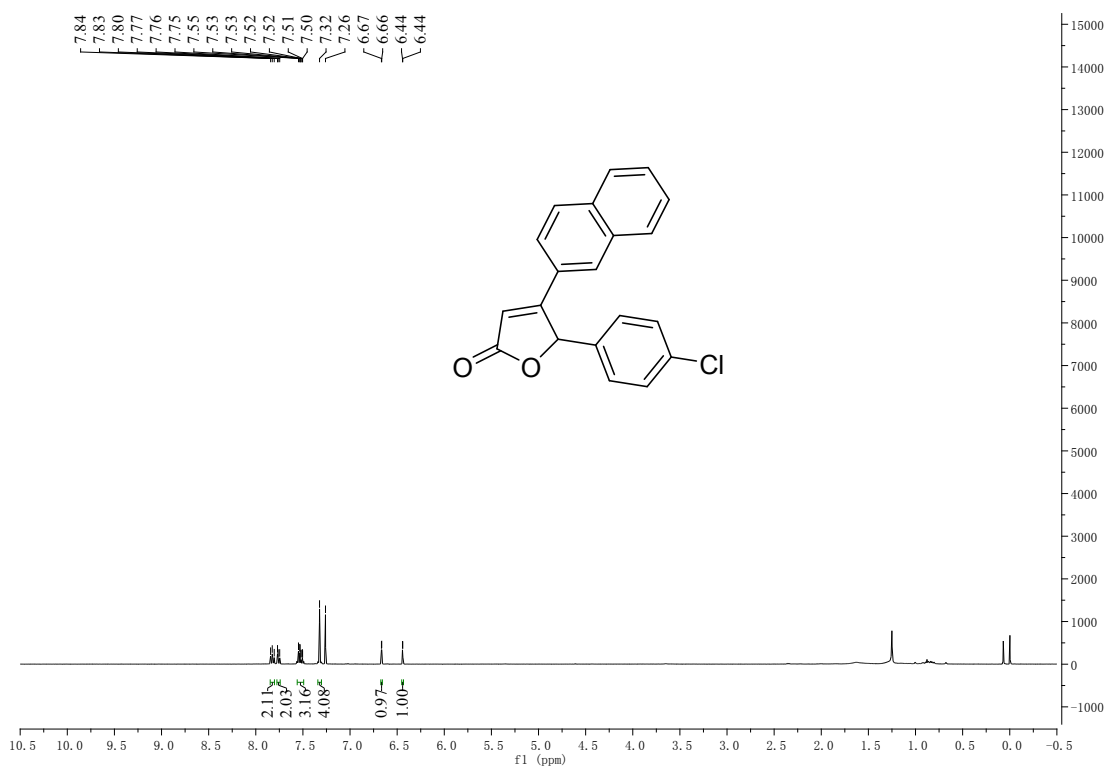
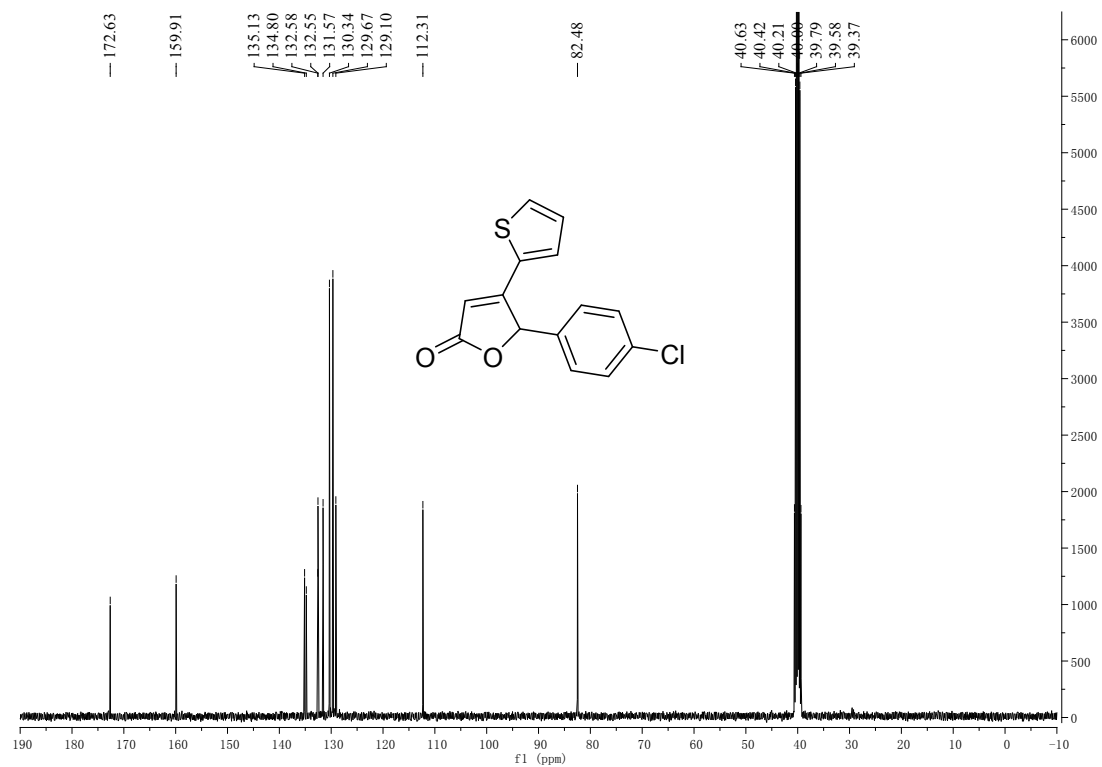


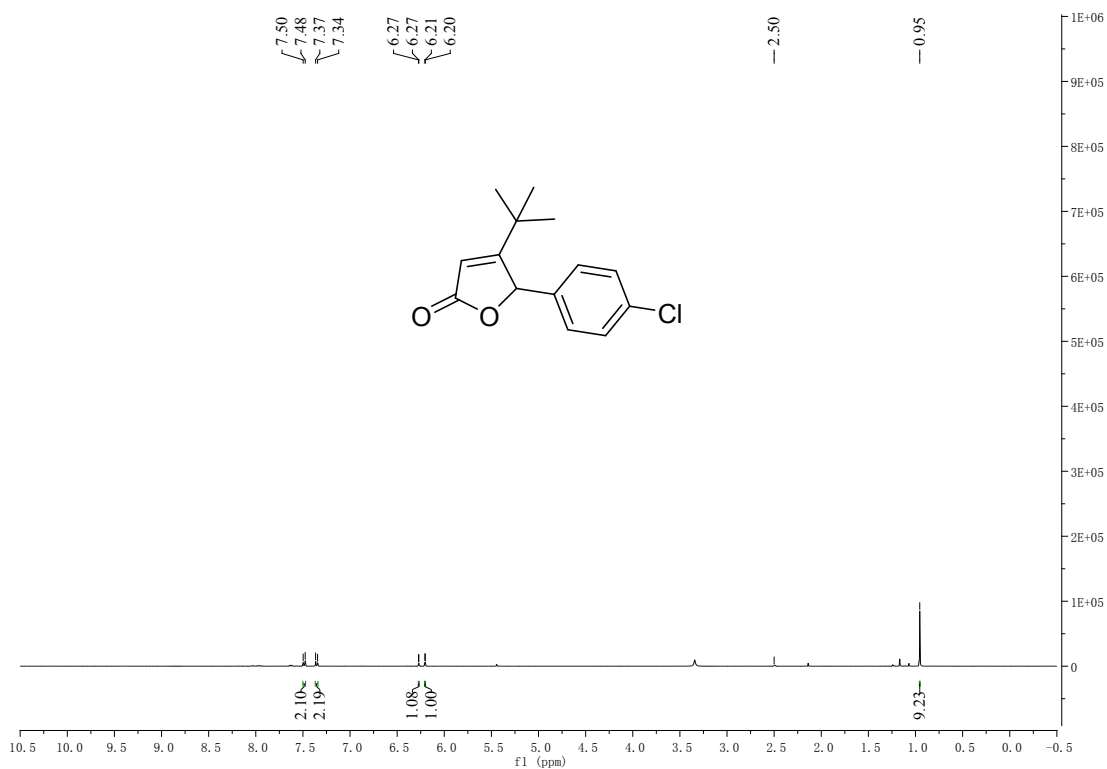
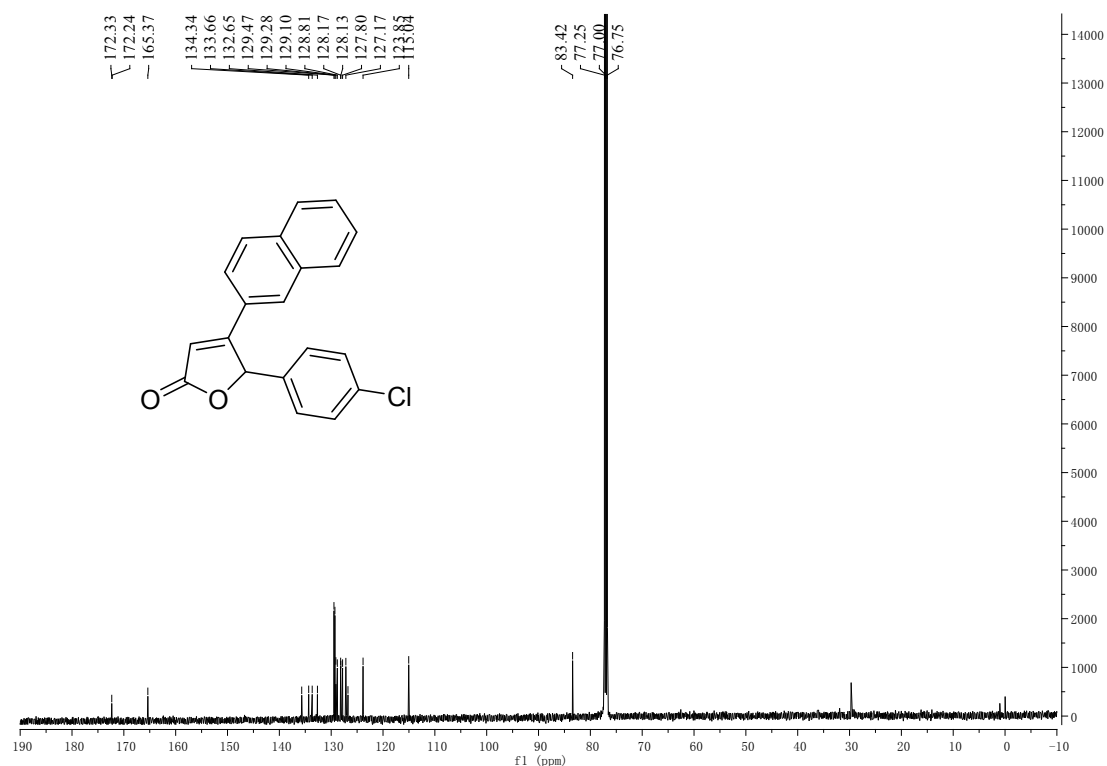


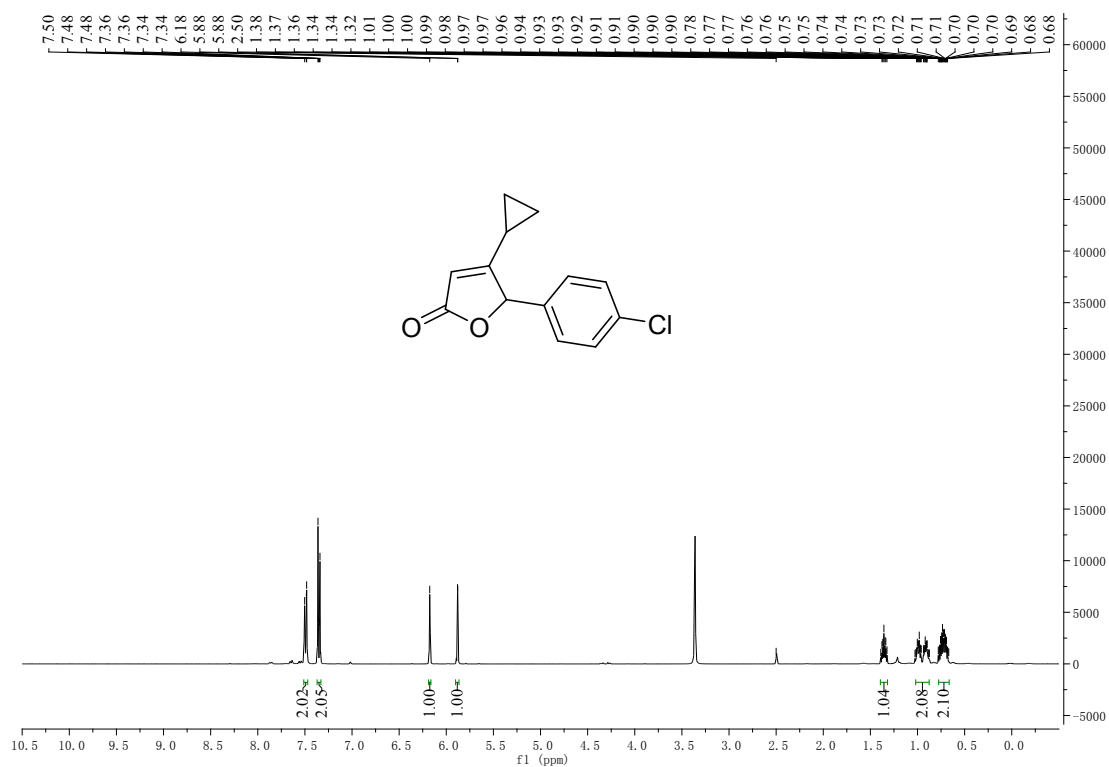
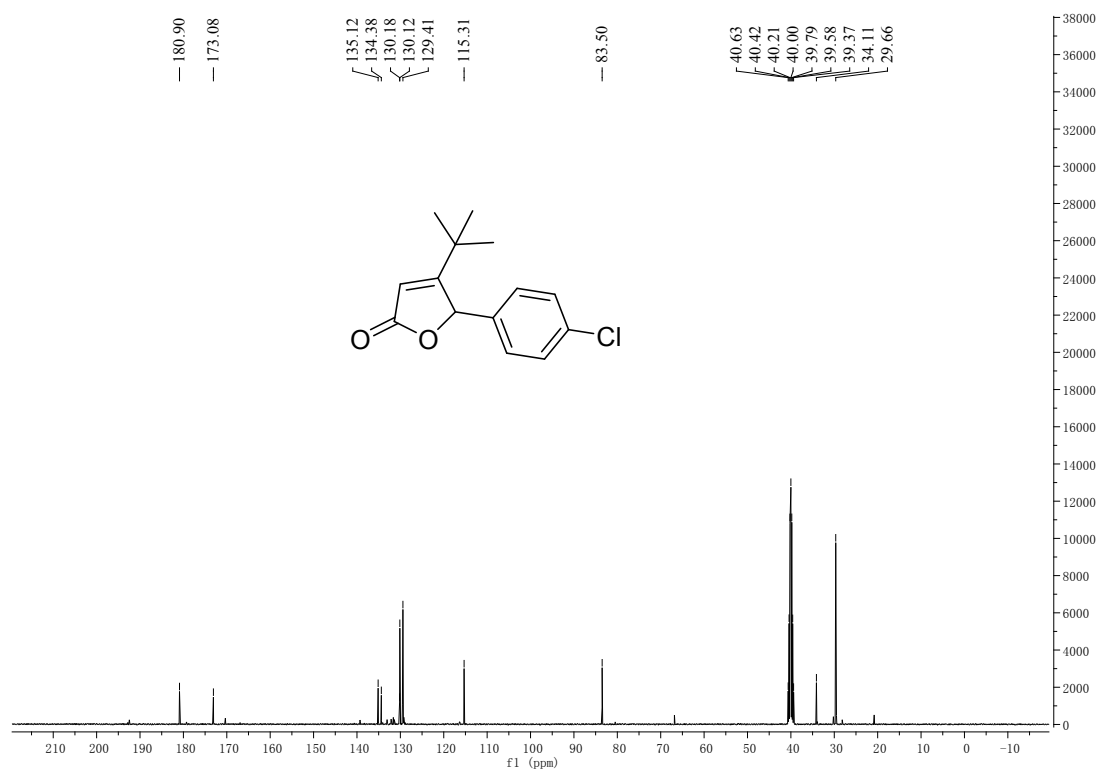


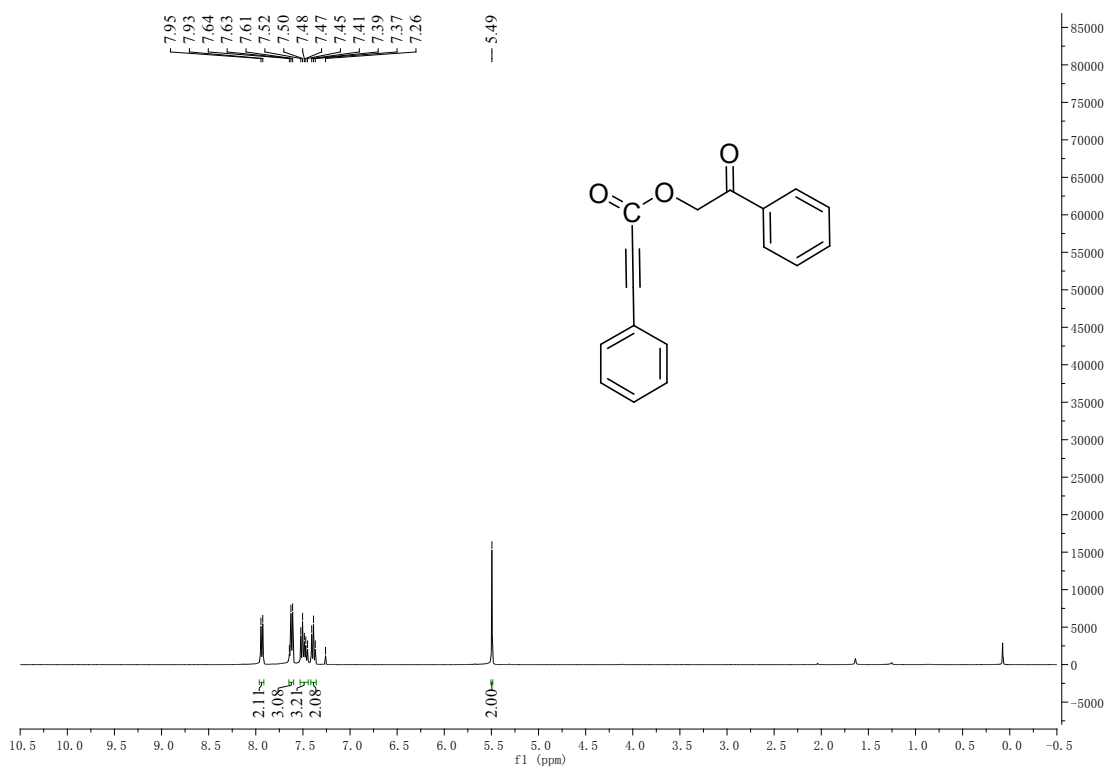
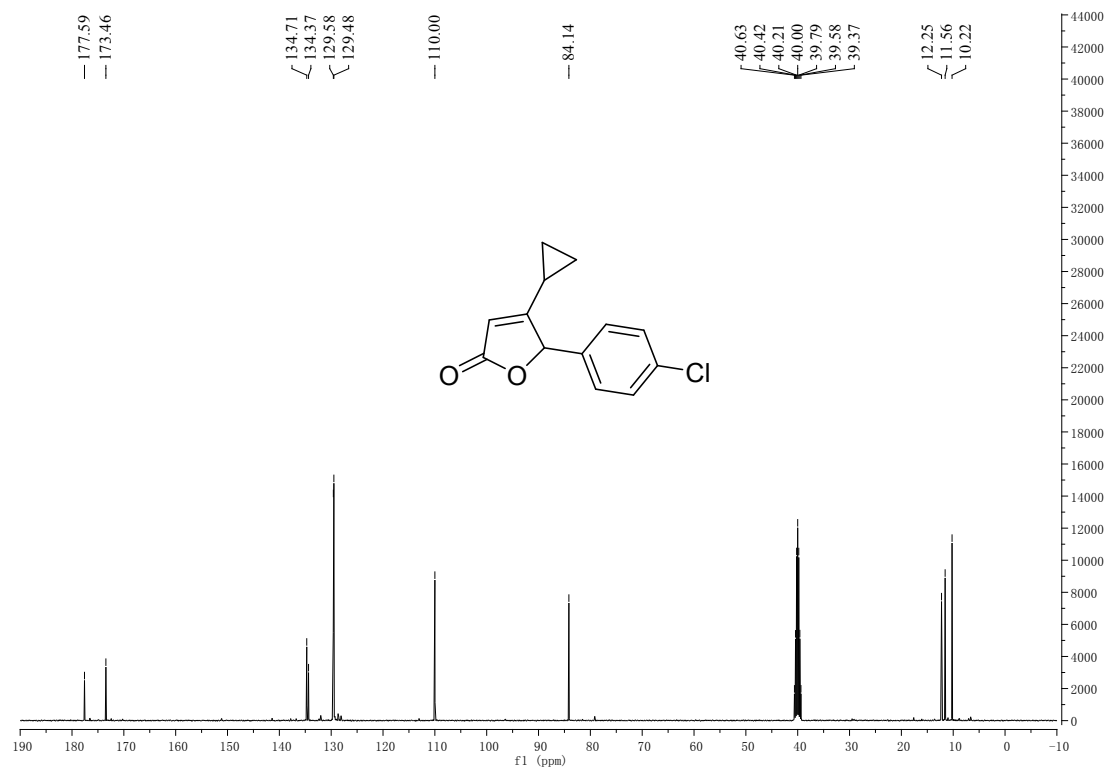


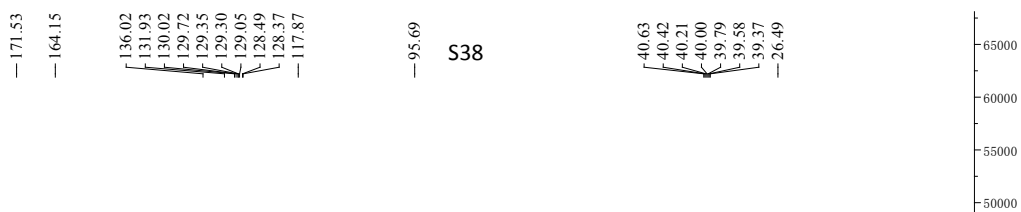
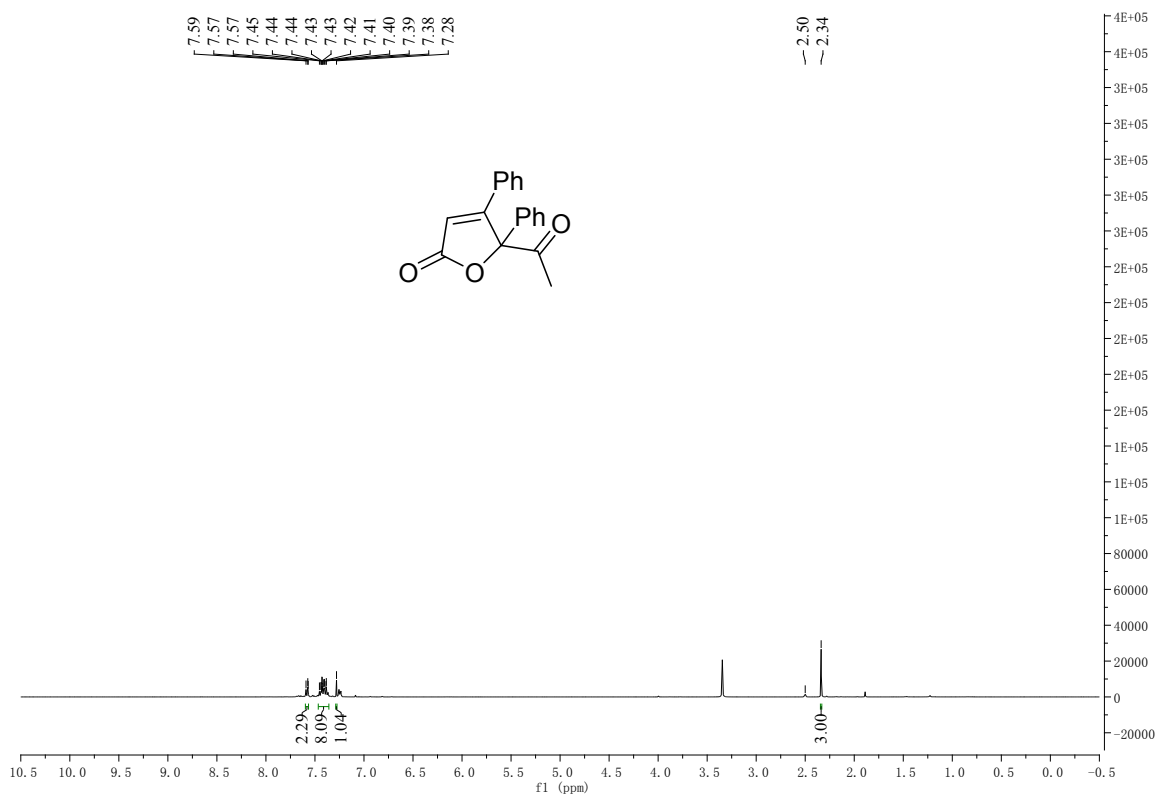
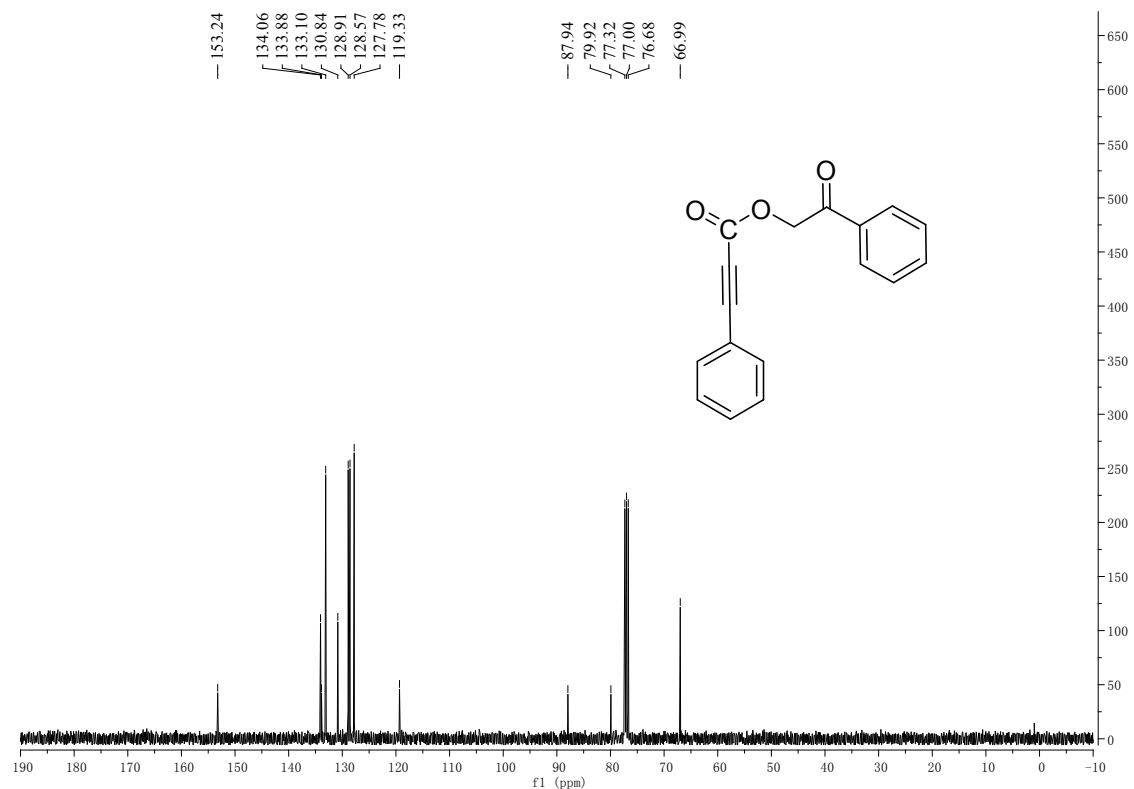


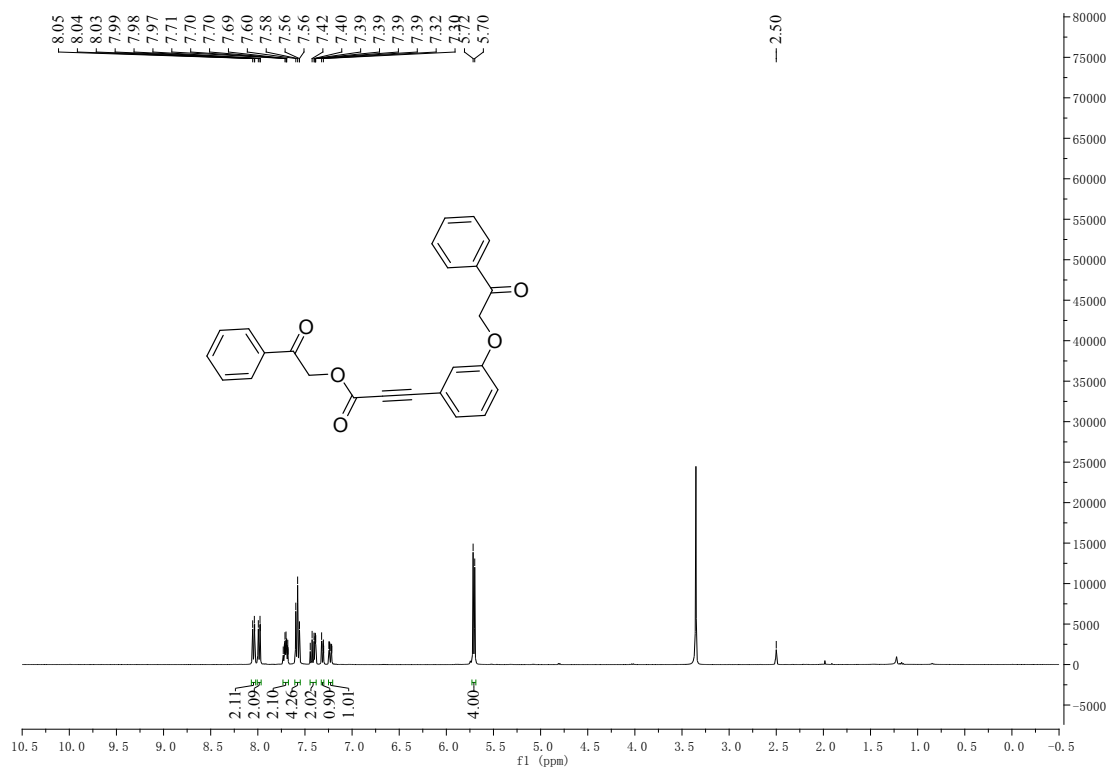
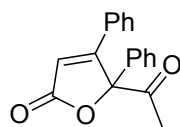


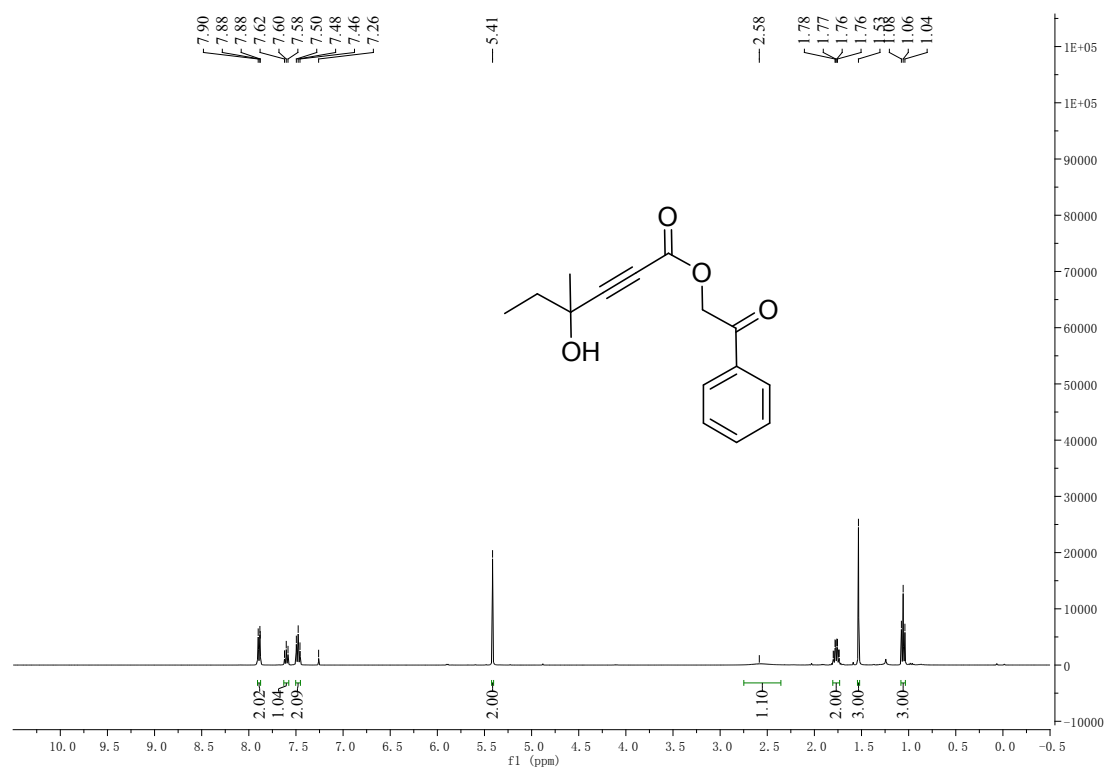
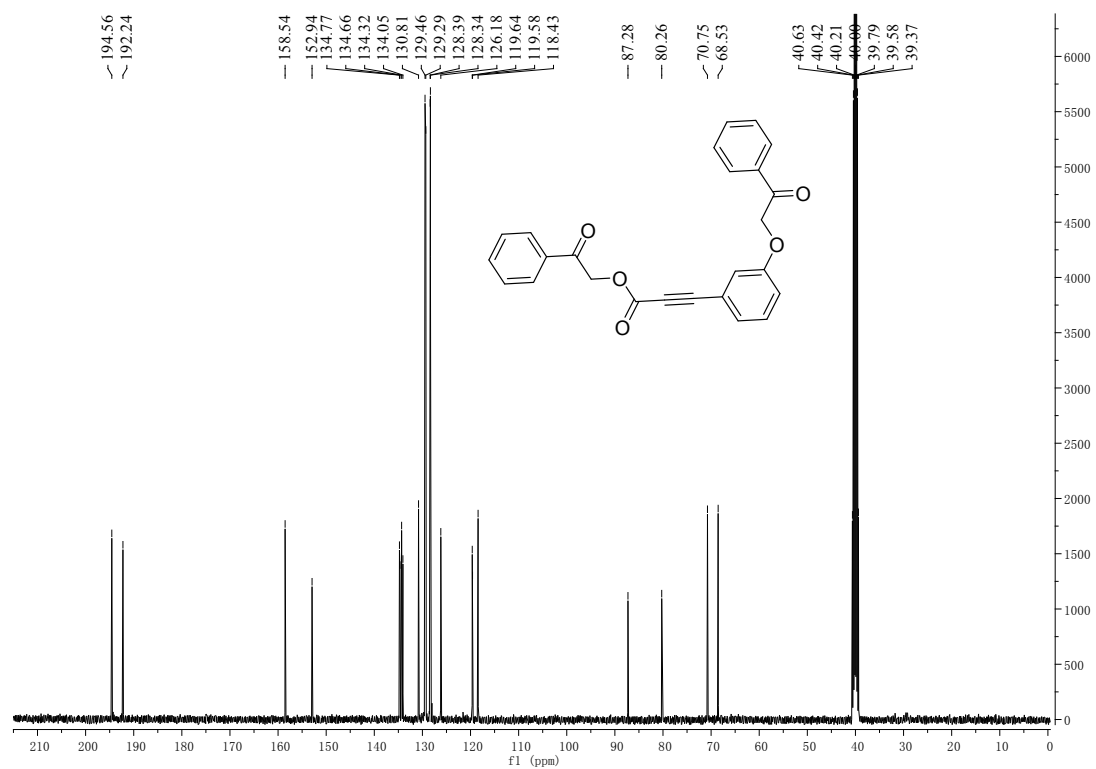


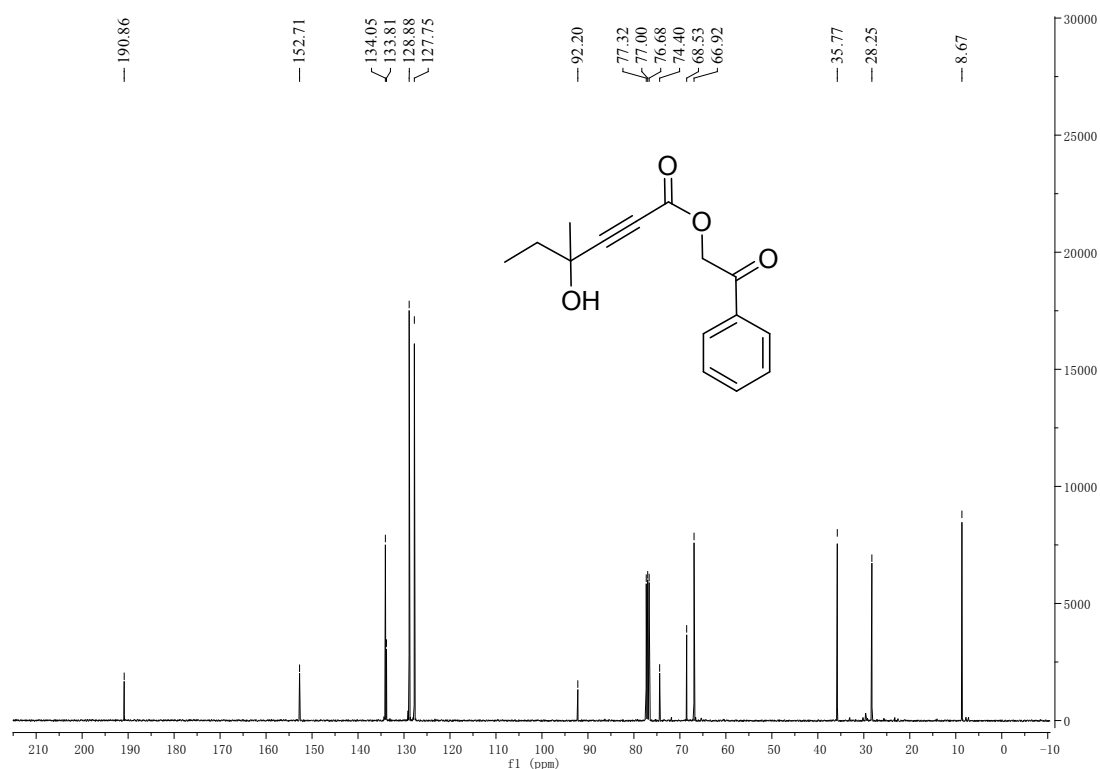












VI. The X-ray Crystal Structure of 4Phenyl-5-(*p*-tolyl)furan-2(5*H*)-one (CCDC 1457861).

